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The Journal of the Society of Dyers and Colourists

Volume 75 Number 6

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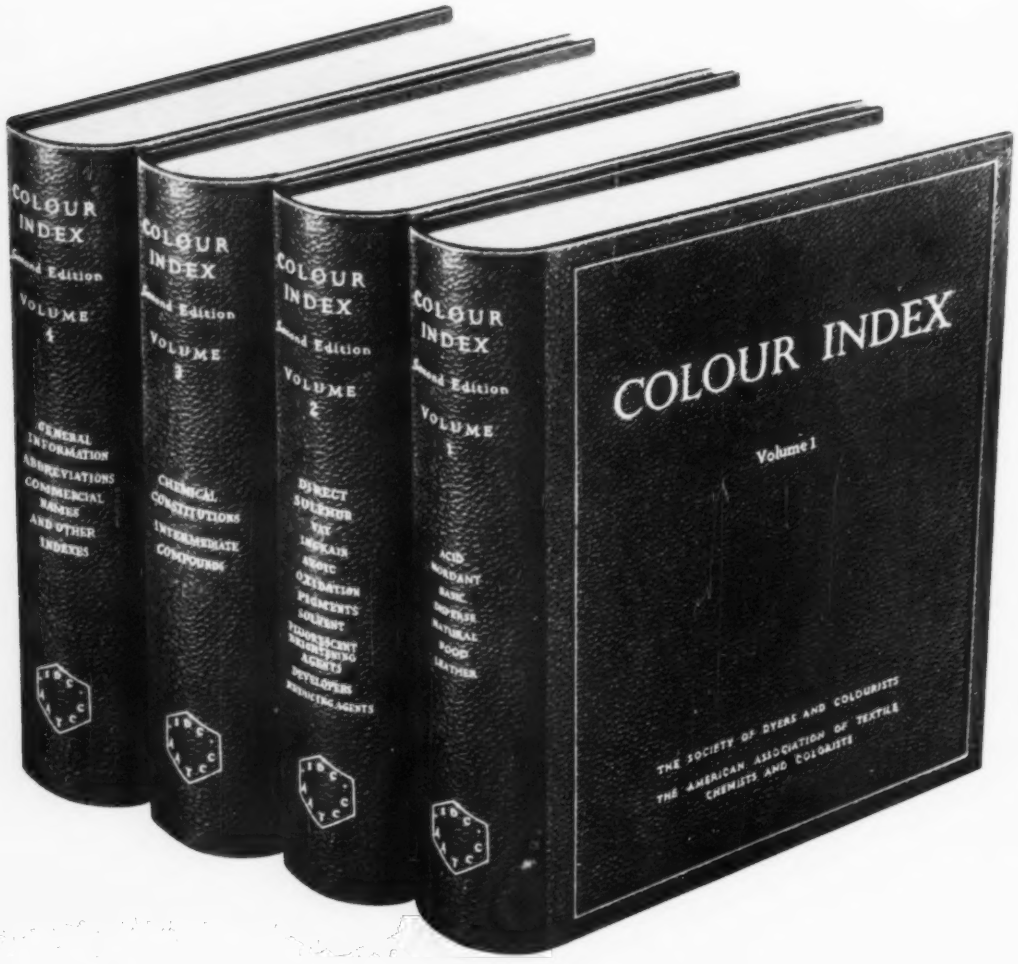

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Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1–10 of the January 1959 and pages 509–516 of the July 1958 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Dyeing Unions containing Acrylic Fibres — *B. Kramrisch*

The Dyeing of Polyester Fibres and Blends — *H. W. Partridge*

The Finishing of Fabrics containing Wool blended with Terylene or Acrylic Fibres — *C. S. Whewell*

EXPLANATORY PAPER ON MODERN THEORY

Surface Activity, Solution, and Adsorption — *C. H. Giles*

FORTHCOMING MEETINGS OF THE SOCIETY

Friday, 23rd October 1959
LONDON SECTION. Seventh London Lecture. Waldorf Hotel, **London W.C.2.** 7 p.m.

Friday, 12th February 1960
LONDON SECTION. Annual Dinner and Dance. Waldorf Hotel, **London W.C.2.** 7 for 7.30 p.m.

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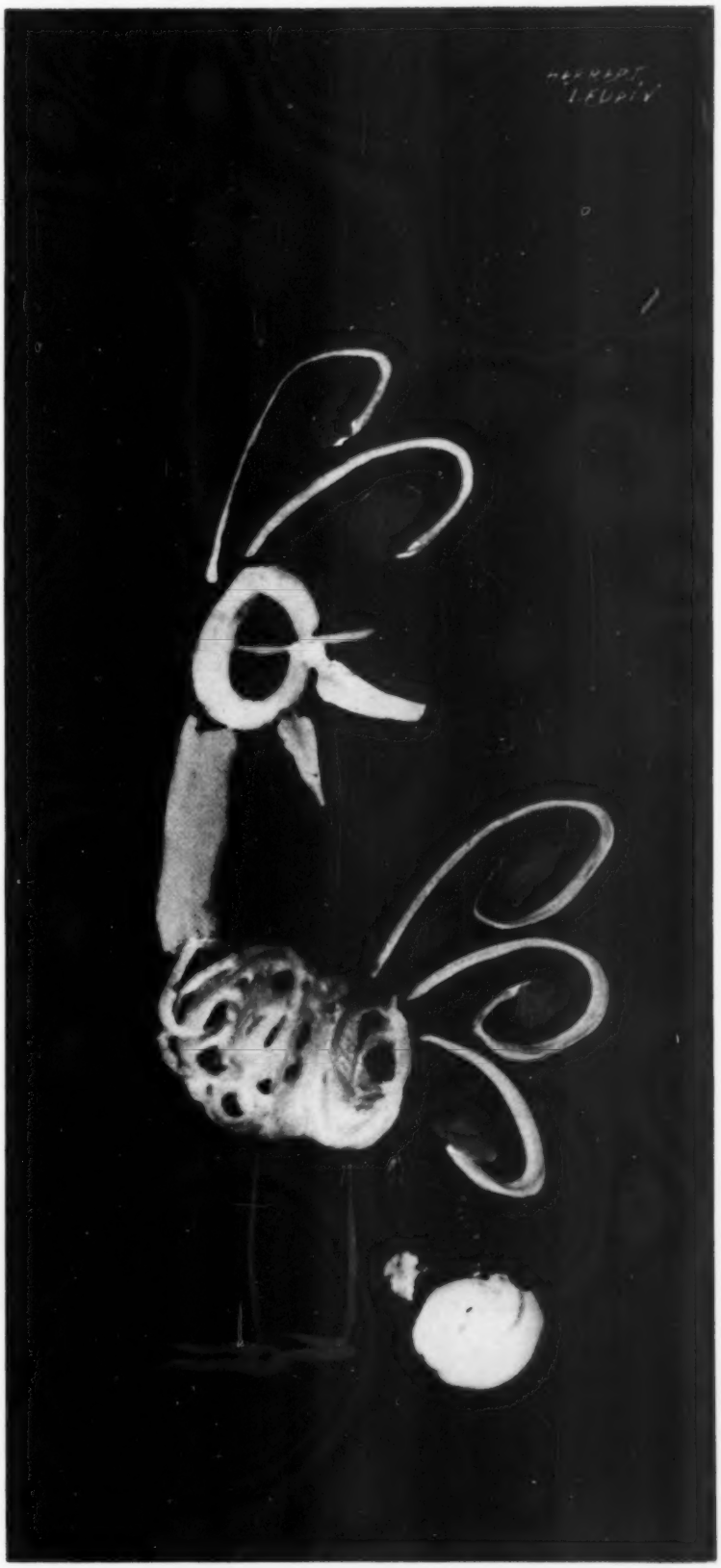

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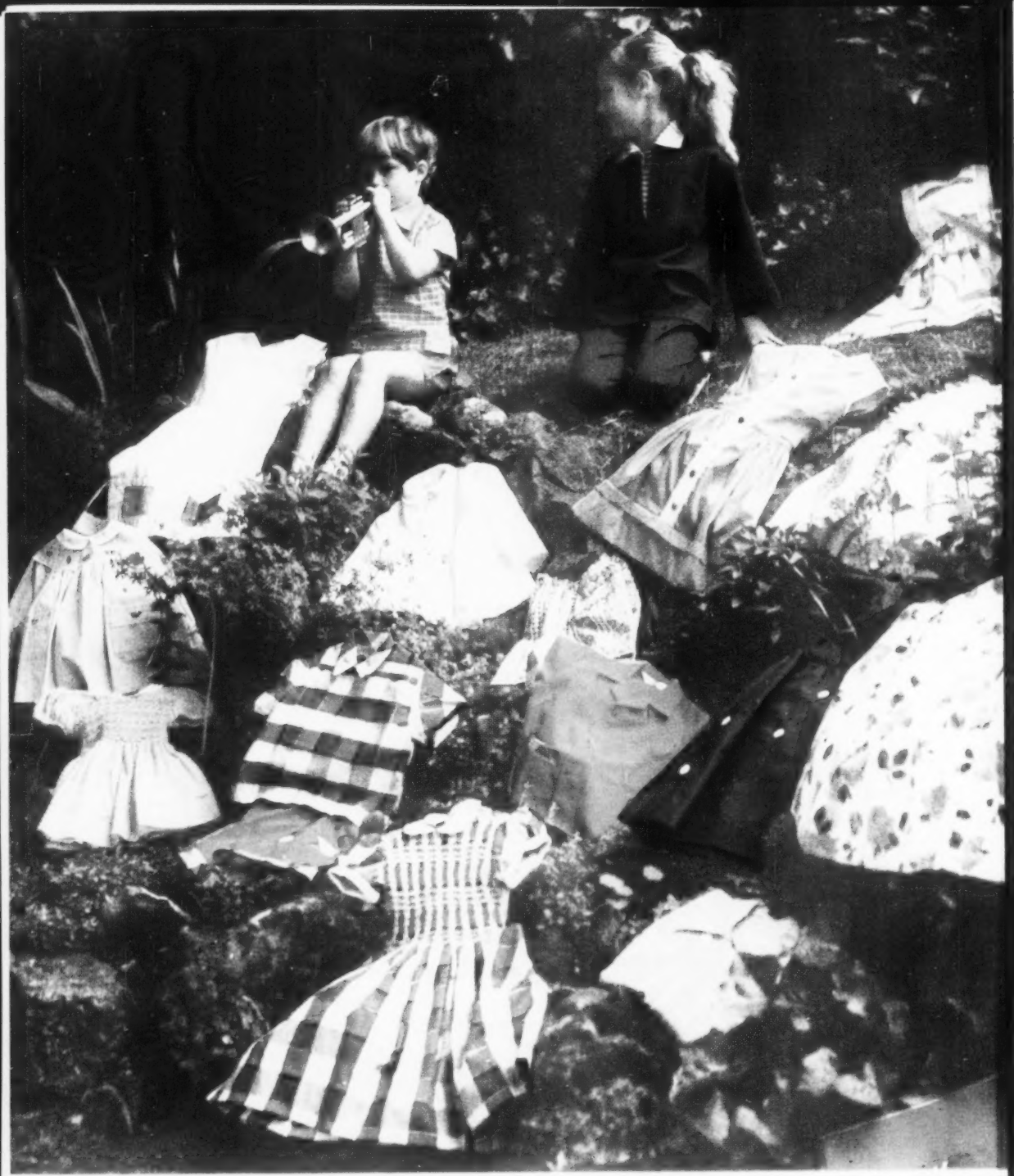

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THE JOURNAL

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Volume 75 Number 6 JUNE 1959 *Issued Monthly*

Proceedings of the Society

SYMPOSIUM ON "THE DIAZO REACTION TODAY"

The Society held a One-day Symposium in the Reynolds Hall of the Manchester College of Science and Technology on Friday, 26th September 1958, with the object of commemorating the Centenary of the Discovery of the Diazo Reaction by Peter Griess. The arrangements for the Symposium had been undertaken by the Manchester Section of the Society.

MORNING SESSION

Chairman—Mr. JOHN BOULTON (*President of the Society*)

Peter Griess

JOHN BOULTON

In celebrating the Centenary of Peter Griess's remarkable discovery of the diazo reaction, we are to hear five papers and a closing address. The reaction itself is so far-reaching in significance, and the life and times of its discoverer are so rich in incident and history, that there should be room for much more information and discussion than can be included in a one-day symposium. Nevertheless, in introducing the day's proceedings at any length I put myself in danger of poaching on preserves intended for lecturers better qualified than I to talk in all their respective spheres.

In the new edition of the *Colour Index* the dyes which have an azo grouping in their constitution form by far the largest proportion in all sections, taking into account all chemical types of colouring matter. Apart from the huge number of azoics (in which Griess's reaction is caused to take place on the fibre), there are very nearly 2,000 azo dyes sold commercially whose constitution is known. The number actually made by chemists in the last 100 years is very many times as great. Less than 30 years after Griess's original discovery, i.e. 70 odd years ago, nearly 10,000 individual coloured azo compounds were covered by patents, most of them German.

It is, of course, as a result of this massive inheritance that we dyers and dyemakers claim Peter Griess for our own and that it falls to us to celebrate his work by holding this Symposium. We shall hear from our lecturers something of every aspect of the diazo reaction.

What we know already and what we will hear are sufficient to make us realise that Peter Griess was one of the greatest chemists who ever lived. But I think it deserves saying that there is a great deal more to his work than this massive consideration of the dyes containing the chemical grouping which he discovered and discovered how to achieve synthetically. In the making of dyes of every class (including those in which there are no azo groups at all), of drugs and pharmaceuticals, raw materials for the polymer industry, and the general gamut of organic chemicals, it is necessary to make use of Peter Griess's discovery of the diazo reaction in order to produce intermediates, although there may be no nitrogen at all in the final product.

It should not be overlooked in our assessment of Peter Griess's discovery that the simple diazonium salt itself can be converted into a wide range of substituted aromatics, to which, even now in a great many cases, his reaction is the only route. One cannot begin to count, or even determine the order of, the number of vital intermediates to which this has applied in the last 100 years and still applies.

All great discoveries have the indefinable flavour which comes either from utter simplicity or from utter unexpectedness. What has to be remembered about the Griess reaction is that it has probably led to the synthesis of more new compounds than any other single reaction discovered in the realm of organic chemistry, yet it makes use of the most inert of all common chemicals—nitrogen. It is this circumstance more than any other that lights up Griess's discovery with the indescribable touch of genius.

We shall hear from our first lecturer something about the man himself. All I would like to say is that, in common with so many other geniuses

and in contradistinction to the popular view that the genius is often a one-sided oddity, Peter Griess was a many-sided person with a thoroughly rounded personality and character.

From being sent down from Marburg University—for what would appear to be student offences perpetrated in, around, and because of the beer cellars of the area—to become the most sober and coldly intellectual of men faced accidentally with a life as a brewery chemist; at the same time to apply his genius to something entirely different and get an F.R.S. for diazo chemistry; and yet to harp back as he did from time to time to allied problems, such as the effect of vibration on the keeping qualities of wine in the City of London: all this shows not merely Griess's manifold interests, but also his many-sided character as a man, and is outward evidence of a complex and subtle mind. Again, he longed to return to his native land; yet he married an English lady and had a full and happy home life in the English Midlands.

To long, as Griess had longed, to return to Germany, and yet to stay on in England and declare that he found our music and our artistic interests to his taste, was to live with an apparent paradox out of which many of his contemporaries from Germany extricated themselves to go back and, unhappily, spread the view that England was a "country of shopkeepers". Peter Griess, in spite of his great love of all things German, was one of the great men who discovered us, the English, and reached the right conclusions about us.

The Life and Times of Peter Griess

W. H. CLIFFE

Until he was 28 years old Peter Griess betrayed no sign of his latent genius for chemical research. As a student at Marburg University, he at first showed little interest in science and preferred the society of irresponsible and pleasure-seeking companions. His discovery of diazo compounds in 1858 attracted the attention of others and led him to write the first of more than 140 contributions to chemical literature. Almost the whole of his work on diazo compounds and their reactions, and on azo dyes, was carried out in England, first at the Royal College of Chemistry and thereafter during his 25 years as chemist to Samuel Allsopp & Sons at Burton-on-Trent. Griess's work is sketched against the background of the times. He is seen as a nostalgic, lone worker, watching the growth of a great industry in which he had no part but which developed by organised research based on his own pioneering efforts. Honoured in this country and abroad during his lifetime, Griess died suddenly in 1888.

In our twentieth-century atmosphere of political mistrust the word "revolution" has something of a sinister sound. True enough, in our still imperfect state of social development, revolution and violence can all too often mean much the same. But revolution need not mean rebellion. It properly signifies change, and, moreover, change which is rapid and radical. It may be a change which wipes out an age-long condition of affairs. In the wake of one revolution may come another. The Industrial Revolution, which historians have called "the greatest single event in the world's history", centred round mechanical invention—spinning machines, power looms, steam engines. It brought an economy based on coal and iron, and from this arose a field of technics founded on coal as a chemical raw material and on theoretical knowledge. That in itself was a revolution—a Chemical Revolution, and more particularly an Organic Chemical Revolution. Like the Industrial Revolution, of which it formed part, it was initiated by invention, and invention was its driving force. It passed through successive phases of development of increasing complexity. The great names of the mechanical age—Hargreaves, Arkwright, Crompton, Watt, Stephenson, Bessemer, Nasmyth—were matched in the organic chemical age by Mansfield, Perkin, Hofmann, Nicholson, Caro, Martius, Williams, Witt. There are other names on that illuminated scroll of fame, and among them is one in letters of burnished gold and, most appropriately, in the brightest and most diverse colours, that of Johann Peter Griess (Fig. 1). An imperishable name, for, wherever colour is applied today by the art and science of man, no small part is a debt to Griess and his work of one hundred years ago.

He belongs to a vanished age. There could be no Griess today. He was virtually an amateur scientist, in the sense that the work which brought him fame was completely unrelated to that upon which he relied for his bread and shelter. But Joule was a brewer and Nasmyth was an astronomer. There is something about England and the English way of life which is oddly conducive to scientific amateurism. Why it should blossom more fully and bear a richer fruit here than abroad is a matter for speculation.

In Central Germany, at the foot of the wooded basalt slopes and to the south-east of Cassel, lies the village of Kirchhosbach. It can be reached by rail today, but in the early years of the last century it was an isolated community of little more than five score inhabitants. It was here that Johann Heinrich Griess and Catharine Elisabeth Gliem married and set up home together. Heinrich Griess was, perhaps, the German equivalent of the English yeoman, neither poor nor rich. He lived in one of the best houses in the village (Fig. 2), and it is said that he built it himself with timber cut from his own small wood. He ploughed and sowed his own land, and he owned the village smithy. In primitive rural communities at that time, child mortality ran high. The Griess family was not spared, for of a large number of children only one survived. He was Johann Peter Griess, born on 6th September 1829.

One senses from the only account which is left to us that young Peter had a good home. What more natural than to be looked upon as the heir

to the family land and business? But that was not all that his father wanted. He thought that by careful education his son could rise to a higher social plane. Peter's first lessons were from the village school and the village parson, but in his father's fields he showed small liking for agriculture. With a book in his pocket Peter could forget the plough, and often did.

When Peter was 15 or 16 years old his father sent him to an agricultural school of good repute. It was on the Beberbeck estate in the middle of the Reinhardswalde, not far from Hofgeismar. One of the pupils, named Bierschenk, wrote to Professor R. Schmitt in Dresden many years later—

> I well remember how Griess arrived, accompanied by an old maidservant struggling with a basket holding his clothes. They had walked every yard of the way for 18 hours. Griess looked a real farmer's boy. Farm clothes, farm manners. His home was only 1½ hours' journey from mine, so we sat together for meals. He had to put up with a good deal from the other boys, and their teasing well nigh drove him to distraction. It was a month before his teacher took any notice of him, but his diligence and knowledge of botany, which was far greater than ours, soon marked him out.

Griess stayed there only for a year before moving to the Cassel Technische Hochschule. We do not know why he left. It certainly had nothing to do with his relations with his school fellows, and one would not go to Cassel for tuition in agriculture. He must have had other motives.

The Cassel Technische Hochschule was the forerunner of the great Technische Hochschulen at Berlin, Aachen, Munich, Dresden, and Karlsruhe. When it was founded in 1831, Wöhler was its first professor of chemistry, but he moved to Göttingen in 1836 and was succeeded by Bunsen. Two years later Bunsen took the chair at Marburg and was followed by Winkelblech, who probably gave Griess his first introduction to chemistry. There is no reason to think that Griess showed any interest in either chemistry or physics. In fact, very little is known of him at this time, and it is not even certain when he left. We do know, however, that he had a short spell of military service. He passed an examination which carried with it the privilege of serving for only one year. He became a Hussar, probably at either Cassel or Hofgeismar, which both had regiments of Hussars, but Griess was no soldier. Fortunately, his father had done well out of timber, and after a few months he bought his son's freedom for 600 thalers.

Griess was then ready to begin his academic studies, and in the autumn of 1850, at the age of 21, he entered Jena University. Why Jena and not the state university of Marburg is not clear. Perhaps his father had something to do with it, because Jena incorporated an agricultural college, although there is no reason to believe that Griess took advantage of it. All we know is that he enjoyed the life and attended Schleiden's botany lectures.

In the autumn of 1851 Griess moved from Jena to Marburg. It looked then as if he would take up the humanities. Most of his time was spent in attending lectures in philosophy, logic, and psychology. Is it possible, one wonders, to detect some foreshadowing of his future scientific career? He was specially interested in the lecture experiments of the young physicist Hermann Knoblauch, who had reached Marburg from Berlin in 1849.

From descriptions by his fellow-students it seems that Griess still clung to his rustic mannerisms, but his personality and character were changing fast. His high spirits, ebullient nature, and delight in pleasure-loving companionship admitted him to the ranks of the more irresponsible elements of the university. Indeed, they sought him. The bars and beer gardens of the town knew them well. There were conflicts with academic and civic authorities. More than once Griess was left to reflect in the university lock-up. Then matters reached a head. On 1st December 1853 Griess was rusticated for breach of the peace.

Griess was then obliged to choose between idleness and study elsewhere, so he went to Munich to hear Liebig lecture. Munich was then in the grip of cholera, and perhaps that was why Griess did not stay long. Part of his time was spent at home, the rest in the town of Marburg, where once again he found himself behind bars. In the spring of 1855 Griess was re-admitted into the University of Marburg to begin his tenth term. His patient father no doubt thought it was high time his son settled down to serious study, but Peter was not yet ready.

At Marburg there was a so called "Progress Union", quite separate from the Students' Union, which it did not recognise. It was formed in 1846 as a counter to the more unpleasant abuses of the student corps. Its original name was *Franconia*. When the iron hand of authority was felt in Marburg, this body attracted a certain type of student. Its members probably thought of themselves as freedom-loving. The academic authorities would have used another expression. The two unions often fought, though duelling was scrupulously avoided, and "Franconia" prudently changed its name and quarters as often as convenient. Griess, of course, was a member, and there were many tales of him at this time, but whether based on fact or fiction is hard to decide. He must surely have drawn the line somewhere, because window-breaking and pulling down bells were expensive pastimes, and his father's resources were strained to breaking point. Griess began to know poverty. He was driven to borrow money, and even clothes, from his friends, and to look to them for shelter when he lost the very roof over his head.

This sorry state of affairs had the belated effect of bringing Griess to his senses. He perceived that riot and roistering were poor foundations upon which to build a career. In his twelfth term he settled down to study chemistry, but, it must be admitted, without achieving very much.

At the end of the summer term of 1856, the Oehler Tar Distillery at Offenbach-am-Main, one of the oldest factories of its kind in Germany, announced a vacancy for someone with chemical training. After some struggle with his conscience, Kolbe made a recommendation, and Griess began his first employment. Had he remained there, it is probable that chemical history would have taken

a different course. As it was, there was an accident involving benzole and sulphuric acid which reduced part of the factory to rubble. In modern parlance, Griess became redundant. It was a very different Griess who returned to Marburg in the summer of 1857. He was a changed man. Separation from his student intimates, factory discipline, the chance to earn money—all these perhaps gave him a sense of purpose. In the laboratory at Marburg he worked as he had never worked before, under the guidance of the first assistant, Dr. Rudolf Schmitt, who later became professor at Dresden. Schmitt said in later years that Griess's perseverance was remarkable. Proof against the enticements of his former companions, he was first in the laboratory, last to leave. What remained of his Offenbach earnings, together with what his father could spare, cleared his debts but left him in such a state that, when an accident with nitric acid damaged his trousers, he could not afford to replace them. But no matter, he had a long smock.

Griess was then 28 years old, a mature man with an uncertain future and a shallow purse. If his precarious position troubled him little, it seemed to have worried Kolbe. In the autumn of the following year, 1858, Professor A. W. Hofmann, of the Royal College of Chemistry in London, visited Kolbe at Marburg. In later years Hofmann recalled that visit in substantially these words—

> On one of our many walks in the district Kolbe first spoke to me of Peter Griess. He praised his energy and observational powers, and his delight in scientific research. "The material circumstances" he said "in which he studies are most unfavourable. His father is a simple countryman who can no longer support him; he must make every effort to be independent. I would like to give him a post in my laboratory if one were vacant, but there is no prospect. Could you perhaps take him to England as your assistant?".

But Hofmann, with a shrinking budget, also had no vacancy. When he retired to rest that night he found in his room an open copy of the April issue of *Liebig's Annalen*. The title of the paper, which he was clearly intended to read, rendered into English, was *Preliminary Note on the Action of Nitrous Acid on Picramic Acid and Nitroaminophenol* (Fig. 3). The author was Peter Griess. The events of the next day, which changed Griess's life, must wait. We must look more closely at this epoch-making paper, which, said Hofmann, "contained significantly the programme for a man's whole life's work."

About the year 1848 Piria noticed that aminosuccinamic acid is transformable into malic acid by the action of nitrous acid. Six years later, Gerland, working at Marburg, and hence probably known personally to Griess, isolated hydroxybenzoic acid as the product of reaction of aminobenzoic acid and nitrous acid. Not surprisingly, the reaction seemed to be complex. When Griess returned to Marburg from his first short-lived employment at Offenbach, he turned his attention to reactions of this kind, very likely at Kolbe's suggestion. Sodium nitrite as a source of nitrous acid was unknown at the time. Some years had still to elapse before Martius's discovery of this great boon to the dye chemist. Griess's methods were cumbersome. He generated nitrous fumes by reducing nitric acid with starch or arsenic trioxide. By what strange trick of fate did he choose picramic acid as his starting material? He needed ethanol to dissove it. Ethanol and nitrous fumes give ethyl nitrite, and ethyl nitrite and picramic acid gave a mass of crystals. Those crystals were a modern "philosopher's stone": there was magic in their touch. They masquerade today under the prosaic name of 4,6-dinitrobenzene-2,1-diazo oxide, but the magic is still there. This, then, was the first of an entirely new class of chemical compounds, the diazo compounds. How bleak it sounds to say that Griess discovered a new mode of reaction of nitrous acid! The philosopher's stone which Helvetius claimed to have seen and handled was ordinary enough outwardly, but it gave him pure gold, or so some say. Griess's crystals and their like were to show their magic in yellows and oranges, scarlets and reds, blues and greens. The gold was there, too, but it was to fill the pockets of others.

But, we may ask, why was it not Piria, or Hunt, or Gerland who displayed the first diazo compound? Let Griess give his own explanation. In 1887, on the occasion of the Manchester Royal Jubilee Exhibition, Griess wrote a letter to Watson Smith which contained these words—

> The circumstance to which I was indebted for my success in obtaining the diazo compounds was that of treatment of the amido compounds with nitrous acid in the cold, whereby the immediate conversion of the diazo compounds into other products was prevented, whereas in the earlier experiments of Hunt and Gerland a higher temperature was always attained, and consequently no diazo compound could exist.

Griess was never an ungrateful man, but he forgot to lay a modest offering on the altar of the Goddess of Chance.

Before we pass on we might take a little thought about that term "diazo", which is so familiar now. It arose through Griess's mistaken conception of his reaction. He believed, and obstinately continued to believe for a number of years, that two atoms of hydrogen in the benzene nucleus had been replaced by two atoms of nitrogen. He evolved, therefore, the term "diazo" and used it for the first time in a paper which appeared in the *Proceedings of the Royal Society* for 1857–1859.

We must now rejoin Hofmann and Kolbe at Marburg in the autumn of 1858. The next morning Hofmann met Griess. Thirty years later he recalled his first unfavourable impression. He remembered the pale expressionless features, the closely cropped head, the awkward movements, and a certain ungraciousness of a man who was impatient of interruption. He remembered, too, the faded linen smock reaching almost to the ground, but of the tragedy of the nitric acid and the missing trousers he knew nothing at the time. There is still an echo from the past in Hofmann's own words—

> But my spirits rose when I began to speak about his work. He was clearly pleased that I had read his paper. I was astonished to see a positive transformation in him. He showed me the substances which he had described and others which he had

Fig. 1 — Peter Griess

Fig. 2 — Peter Griess's Home at Kirchhasbach (built in 1831)

Vorläufige Notiz über die Einwirkung von salpetriger Säure auf Amidinitro- und Aminitrophenylsäure;

von *Peter Griefs.*

Wird in eine alkoholische Lösung von Amidinitrophenylsäure ($C_{13}\left(\begin{smallmatrix}H_2\\2\ NO_4\\H_2N\end{smallmatrix}\right)O.\ HO$) ein rascher Strom von salpetriger Säure geleitet, so fällt, nachdem die Einwirkung längere Zeit angedauert hat, ein Körper in messinggelben Schuppen nieder. Dieser läfst sich leicht durch Umkrystallisiren aus Alkohol reinigen. Die Mutterlauge, aus welcher der Körper sich abschied, enthält Dinitrophenylsäure. Ich glaubte, der neue Körper würde seiner Bildungsweise gemäfs die Zusammensetzung $HO, C_{13}\left(\begin{smallmatrix}H_2\\2\ NO_4\end{smallmatrix}\right)O_3$ haben; die Analyse belehrte mich jedoch, dafs sich seine Zusammensetzung durch die empirische Formel:

$$C_{13}H_2N_4O_{12}$$

ausdrücken läfst. Die Verbrennung des bei 100° getrockneten Körpers gab im Mittel:

C	34,2
H	1,1,

die obige Formel verlangt:

C	34,3
H	0,9 pC.

Die nach Bunsen's Methode ausgeführte Stickstoffbestimmung ergab das Verhältnifs des Stickstoffs zum Koh-

FIG. 3.—Peter Griess's First Publication in *Liebigs Annalen*, 106, 123 (1858)

FIG. 4.—Laboratory in which Griess worked at Burton-on-Trent

SUB AUSPICIIS GLORIOSISSIMIS

AUGUSTISSIMI AC POTENTISSIMI DOMINI DOMINI

LUDOVICI II

BAVARIÆ REGIS

COMITIS PALATINI AD RHENUM BAVARIAE FRANCONIAE ET IN SUEVIA DUCIS CET.

IN INCLYTA UNIVERSITATE LUDOVICO-MAXIMILIANEA

RECTORE MAGNIFICO

EXPERIENTISSIMO ET ILLUSTRISSIMO VIRO

JOANNE ALPH. RENATO DE HELFERICH

OECONOMIAE PUBLICAE ET PHILOSOPHIAE DOCTORE OECONOMIAE PUBLICAE ET AUTIS PUBLICORUM REDITUM ADMINISTRANDORUM PROFESSORE PUBLICO ORDINARIO A CONSILIIS AULICIS REGIS BAVARIAE ORDINIS MERITORUM CORONAE BAVARICAE ET ORDINIS EQUESTRIS CUELFICI INSIGNIBUS ORNATO CET.

EXPERIENTISSIMUS ET SPECTATISSIMUS VIR

ADOLPHUS BAEYER

PHILOSOPHIAE DOCTOR CHEMIAE PROFESSOR PUBLICUS ORDINARIUS LAU. RADOLF. CHEMICI CONSERVATOR ACADEMIAE LITERARUM MORAC SOCIUS ORD. BORUSSICI AQUILAE RUBR. CL. IV. EQUES CET.

FACULTATIS PHILOSOPHICAE SECT. II P. T. DECANUS ET PROMOTOR LEGITIME CONSTITUTUS

PRAECLARO ET DOCTISSIMO VIRO AC DOMINO

IOANNI PETRO GRIESS Ph. D. S.

RHEINHESSIACHENSI

PROPTER EXIMIA DE CHEMIA ORGANICA MERITA ATQUE AD MUNOPIAM QUINQUAGESIMI NATURAE SCRUTATORUM CONVENTUS CONSERVANDAM

DOCTORIS PHILOSOPHIAE GRADUM HONORIS CAUSA

DIE X MENSIS NOVEMBRIS ANNI MDCCCLXXVII

EX UNANIMI ORDINIS PHILOSOPHORUM SECT. II DECRETO CONTULIT.

IN HUIUS REI TESTIMONIUM HOC PUBLICUM DIPLOMA SIGILLIS MAIORIBUS REGIAE LITERARUM UNIVERSITATIS ET FACULTATIS PHILOSOPHICAE ADIECTIS FACULTATIS EIUSDEM DECANUS ATQUE RECTOR MAGNIFICUS ET SECRETARIUS UNIVERSITATIS IPSI SUBSCRIPSERUNT.

FIG. 5.—Certificate from the University of Munich conferring on Peter Griess the Honorary Degree of Doctor of Philosophy (1877)

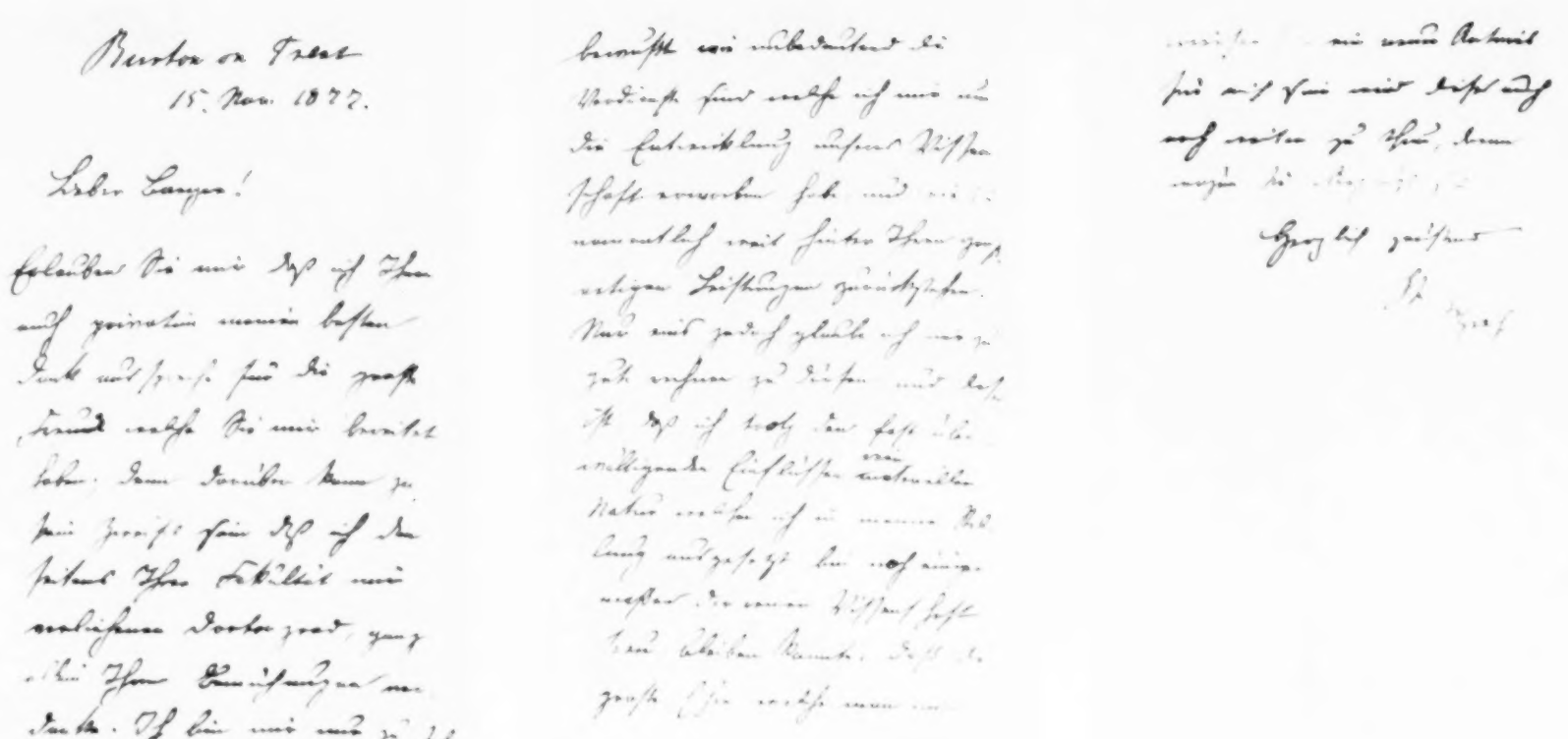

Fig. 6.—A Less Formal Letter from Griess to Adolf Baeyer giving Thanks for the Award of the Honorary Degree

> prepared since the publication of his paper. What struck me was the confidence and precision with which he spoke, so different from the awkward conversation of before. I tried to lead the talk into other fields, but he soon reverted to his new reaction. I followed his words closely. My unfavourable impression of him had already gone. The difficulty of appointing a supernumerary assistant in my laboratory was dispelled, but we parted without any definite arrangement.

Thus wrote Hofmann. Four weeks later Griess arrived in London. We must try to visualise him on that fateful morning as he made his way along Oxford Street to the College doors. We are told that over his sea-green trousers he wore a reddish-brown greatcoat with a red knitted scarf, surmounted by an extraordinary top-hat of a kind which had long since disappeared from the streets of London. Is it surprising that he was refused admittance to the College? He was saved only by his impatient shout: "Ich heisse Griess und bleibe hier!"*.

In its heyday the Royal College of Chemistry was a powerful force both here and in Germany. In some measure it owed its existence to Revolutionary France. If that should seem surprising, let us look back awhile and try to trace the thread. Those who have glanced over the chemical textbooks of Europe cannot help noticing how the false ideas of transmutation lingered on in Germany long after they had been discredited in England and France. Liebig's remarks on the backwardness of chemistry in his own country when he was a boy were scathing. It seems that even at so late a date professors indulged in magic and speculation. Wurzer at Marburg was one of them. Liebig's explanation was that—

> . . . long years of war had undermined the well-being of the people, and external political pressure had brought in its train the desolation of our universities, filled men with painful anxiety for many years, and turned their desires into other directions.

In their struggles for emancipation from foreign domination, the Germans developed a social philosophy in which there was no place for science. The new chemistry inspired in England, Sweden, and France had no counterpart in Germany. Hence, when Liebig began to study he was almost driven to Paris.

The social forces behind the French Revolution implanted in the minds of French chemists an earnest belief in the power of science to improve mankind's condition. Lavoisier died on the guillotine, but there were other powerful intellects. Liebig absorbed their ideas and carried them back with him to Giessen, where he founded his famous laboratory in 1824 when he was 21 years old. There he taught the methods and spirit which he had learned in France. Germany was changing then. The non-industrial feudal society was crumbling, and Germany was becoming responsive to new ideas. Hofmann was trained in Liebig's laboratory. His father was the architect who designed it. From Liebig, Hofmann absorbed the ideas of Revolutionary France. He believed that chemistry should be pursued for its own sake and should not be exploited for commercial profit. Noble ideas, but they helped, perhaps, to sign the death warrant of the Royal College of Chemistry.

The College, with Hofmann in charge, began its life in 1845 with 26 students housed in temporary quarters in George Street, Hanover Square. It virtually owed its existence to Liebig. Liebig's textbook of 1840—*The Chemistry of Agriculture and Physiology*—and the visit to this country in 1842 of that remarkably inspiring man turned chemistry into a popular science. The direct result was the foundation of the Royal College of Chemistry.

Even then the effects of the Napoleonic wars were still felt. Impoverishment of the soil, falling rents, and the growing industrial population—all prompted the liveliest interest in any method of restoring the fertility of the soil, which meant cheap food, low wages, and low costs. The industrialists and landowners looked for their salvation to the Royal College of Chemistry. The Council of the College itself said in 1848—

> Capital, which has been the boast of this country, can do much, but capital directed by the lights of science may accomplish much more.

The College had no endowments. It lived on subscriptions. Hofmann did what he could. His advanced students were busy analysing water, soils, ashes, minerals, and alloys, or gave service in improving existing methods or processes. The enthusiasm of the landowners, however, began to decline. They expected quick discoveries, and while they chafed and fretted Hofmann pursued his untroubled course, seeking knowledge for its own sake. The College managed to weather the financial depression of 1847–1848, but support continued to dwindle until its extinction seemed well nigh inevitable. It was only by incorporation into the Royal College of Mines in 1853 as the Department of Chemistry that it was saved at all, but the price exacted was not trifling: it became subordinate to professional needs. The death in 1861 of its patron, Prince Albert, robbed the College of social prestige, and interest in organic chemical laboratories began to perish. All that for the sake of £2000 a year! After Hofmann left England in 1865 there was no professorship of organic chemistry in this country until the establishment in 1874 of a chair at Manchester for Schorlemmer.

In London Griess settled to work at once. Problems of the greatest diversity came his way. As Hofmann's assistant he made his contribution to the phosphorus bases. He was always ready to help private firms or public bodies, though not always with success. The decaying stonework in Sir Charles Barry's new House of Parliament faced the College with an insoluble problem, and after some weeks of experiment they beat a retreat to the shelter of their laboratories.

Griess lived happily in London for more than three years, but at first a secluded life. German by birth and German by nature, he found it no less difficult to accustom himself to English ways than to speak the English tongue. In spite of his sociable nature, he shrank from company unless it was predominantly German. It was not strange

* My name is Griess, and here I stay.

that he preferred German food to English fare, and that he found it in a somewhat questionable bar in Soho, where his oddities of dress went unnoticed in that motley crowd of students and political refugees from Italy and Germany. Slowly he changed. With the discharge of his debts in Germany, he began to dress with more care. It was his work which attracted attention and not his appearance. His love of good company and good music surrounded him with friends, many of whom made names for themselves. There was Volhard, later professor at Halle; Leibius, who became Master of the Mint at Sydney; Geyger of the German Patent Office; Holtzmann, private secretary to the Prince of Wales; August Bopp, his closest friend, who was to fill a high position in the Gresham Life Insurance Company; C. E. Groves, later Professor of Chemistry at St. Bartholomew's; and Herbert McLeod, professor at the Indian College, Cooper's Hill. There was Martius, the joint founder of Agfa. Griess knew Hugo Müller, consultant to Thomas de la Rue & Co., always a German, but who so loved the country of his adoption that he virtually died of grief at the First World War.

One hesitates to demolish an attractive story and a popular belief, but the temptation to stray aside for a moment is irresistible. The mention of Thomas de la Rue & Co., long famous for their postage stamps, brings to mind the British penny lilac stamp of 1881. Some think that this is the first commemorative stamp. It is supposed to have been coloured with a lake made from Perkin's Mauve, which was discovered just 25 years before. A not unlikely story, since Perkin knew Warren de la Rue. Both were trained under Hofmann. We tend to repeat what authority states as fact. There is no lack of textbook and published paper to give credence to the Mauve story. But Mr. G. W. Midgelow, of the Dyestuffs Division of ICI, knows that it is a story, for he positively identified the colouring matter of that stamp as the iron lake of cochineal. This has never been announced until now.

While Griess was in London, we may be sure that he did not neglect his diazo work. But that must wait. There is a smell of ale in the air.

At the time of which we are speaking, there was a strong bond between the Royal College of Chemistry and Burton-on-Trent. Burton was then, as now, the centre of the brewing trade, which had been built up over the centuries without aid from science. Burton pale ale was known and enjoyed everywhere.

In 1852 Professor Payen, of the Paris Conservatoire des Arts et Métiers, gave a popular lecture in which he made an irresponsible and mischievous statement: he said that English brewers added strychnine to their pale ale to increase its bitterness. There was consternation at once. The story was repeated by the press both at home and abroad, and there was widespread alarm. Sales dropped. The answer had to come from chemical science, and that was not then to be found in Burton. The chief chemist of Allsopp's Brewery, Dr. Heinrich Böttinger, sought out Hofmann in London and Graham of University College. Together they proved that this story was an utter fabrication. The report which cleared the name of English brewers was published throughout the land and became, in effect, part of a mammoth advertising campaign. It was even printed in *Liebigs Annalen*. That was the beginning of the strong ties between the Burton brewers and the Royal College of Chemistry which did so much in later years to reduce the hazards of brewing.

Ten years after the discomfiture of Payen, Böttinger was at the home of his friend Hofmann. There he met Griess. It could not have been a more opportune meeting. Böttinger needed an assistant. Griess required more than the College could provide. He was not an ambitious man, but at 33 years of age he wanted some prospect of security, and there was small chance of that in the College. Early in 1862 Griess took his leave of Hofmann and travelled to Burton to Samuel Allsopp & Sons, where he was to remain for the rest of his life.

It is strange that we know comparatively little of Griess during the next 25 years, apart from his diazo work. Burton was a small town with a population of just over 18,000. Today it is nearly 50,000. Griess found it a dull town. He took little part in its social activities. The first years were strenuous and exacting. He knew nothing of brewing or the analysis of barley, malt, and hops, and Allsopp's new brewery, erected in 1859, was the largest in Europe. He must have been competent in 1866, for it was then that Böttinger returned to Germany, where he died of cholera in 1874, and Griess succeeded to the post of chief chemist. Sydney Smith said: "What two ideas are more inseparable than beer and Britannia?". And here was a German in practical control of an English brewery!

The departure of Böttinger was a bitter blow to Griess, for he had shared in the family circle and drawn from it a feeling of stability. In all the years he spent in this country he was never submerged in English ways and customs as was Hofmann. He longed for Germany. There is no suggestion that he was influenced by political events, but his homeland was becoming the Germany of Bismarck. There was adventure in the air, and German industry was stirring and growing, helped by German chemists returning home from England. Griess, too, felt the urge to move. He corresponded for many years with Professor R. Schmitt of Dresden, and in one of those letters he wrote these revealing sentences—

> Who can imagine anything better than constant scientific occupation in a town so beautiful as Dresden, and association with those of similar tastes? What would you say if you were in my place? To live in a foreign country in little sympathy with its aims and aspirations, always preoccupied with beer in a town which has little to offer. You must remember that I have almost to steal time for my research work and have no assistant.

Pre-occupied with beer, he said. But what did he do for brewing science? It is hard to say. He published one relevant paper, and that towards the end of his life in association with his assistant, G. H. Harrow, on the occurrence of choline in hops.

Hofmann believed that the terms of Griess's contract forbade him to disclose information. On the other hand, Horace Brown, head brewer at Worthington & Co. and one who helped to revolutionise brewing science, said that Griess, although interested in the application of science to brewing, took no part in contributing to developments, and spent most of his time not devoted to routine activities in those organic researches which we are commemorating today. His value to Allsopps, however, could surely never have been questioned. When that firm was converted into a joint stock company in the eighties, over £100 million was offered towards its £3,300,000 capital. It paid Griess a substantial salary, and when he died he left behind a respectable fortune.

We know almost as little of Griess's private life. After Böttinger's departure for Germany, Griess lived a solitary life in a flat in the town. There is no record of him in the local press. Although he belonged to a flourishing Natural History Society, he seems to have been a passive member. We know that he was a popular member of a dinner club—called the "Bacteria Club"—but when family cares began to appear he seems to have given up attending. "As he brews so shall he drink" said Ben Jonson. But not Griess: he preferred German beer.

This is an attempt to mirror the life and times of Peter Griess, but we must give some thought to his great diazo work. Let us first try to sense the scientific climate of 1862, the year Griess moved to Burton. That was the year of the International Exhibition in London. England, with its wealth of natural resources, led the world in dyes. Perkin & Sons were firmly established at Greenford Green. Successful in the commercial production of Mauve, the first of the coal-tar dyes, they were soon to be in the market with Dahlia, Britannia Violet, and Perkin Green. As yet there was no Clayton Aniline Co., but Simpson, Maule & Nicholson at Locksfield were already making a name for dyes of high quality. About this time Read Holliday and Dan Dawson began their dyemaking activities at Huddersfield. For three years Heinrich Caro had served with Roberts, Dale & Co. of Manchester, and was soon to be joined by Martius. It was Caro, the inventor of the jacketed pan, who made of industrial research what it is today. Friend of England though he was, Caro perhaps more than any other man challenged the supremacy of the British dye industry after his return to Germany to become, in due course, chief chemist and a director of Badische Anilin- und Soda-Fabrik. In this year of 1862 Ivan Levinstein in Germany was thinking of his future, and two years later was to arrive in Blackley to begin his life's work and make history. Despite chaotic patent laws, the dyemaking industry was gathering impetus, to the tune of £400,000 in 1862 even though not long before benzole had cost 20s. a gallon and aniline 20s. a pound. Aniline Yellow and Bismarck Brown had not yet appeared, neither had the Hofmann Violets or Lightfoot's Aniline Black. Lauth's Methyl Violet was known, but four years had still to pass before its commercial production threatened the less fugitive but more sombre Mauve. Verguin's Magenta was three years old, bringing prosperity to some, to others trouble on the plant or in the law courts. Magenta, in fact, was the keystone of the industry for a decade. The "age of Magenta" had dawned, to set later and give way to the "age of Alizarin". These were early days in the great history of organic chemistry, when chemists were still blazing trails without the guiding hand of Kekulé and his benzene theory. By comparison, one is impressed by the elegance and refinement of contemporary physics. The mean free path of molecules had been conceived and calculated, and Maxwell had laid down the fundamental ideas of the electromagnetic theory of light.

In Germany, Liebig's philosophy, which had no sympathy with aggressive capitalistic imperialism, was losing ground and was doomed. Already Humboldt had warned the Germans that in that new age nations who neglected science forfeited power, and his words were not forgotten in the ferment of national revival. So it was that, while Englishmen dedicated themselves to imperial government and the stock exchange, Germany began to focus disciplined energy upon chemistry. In England the Royal College of Chemistry languished for lack of support; in Germany great new institutions arose. The benign motives inspiring German chemistry were subtly obliterated, giving place to a harsh materialistic spirit. The ideals of Liebig and Hofmann were gradually overwhelmed by the hard striving of Baeyer, Fischer, and Duisberg. In 1863, one year after Griess moved to Burton, the first faint shadow of the German chemical colossus appeared. In that year Badische Anilin erected a small factory at Ludwigshafen. They began with 30 workmen. In 1900 they had 6,000.

We have seen that Germany was the birthplace of diazo compounds, and that almost at once they were imported, so to speak, into England. Griess continued his work at the Royal College of Chemistry, preparing a large number of diazo compounds and examing the effects of other reagents upon them. By 1860 he had already demonstrated the formation of halogen compounds by replacement of the diazo group by chlorine, bromine, and iodine. He obtained and recognised the diazoamino derivatives of aminobenzoic, aminotoluic, and aminoanisic acids, and he observed the formation of diazoaminobenzene. Simpson, Maule & Nicholson are credited with the first manufacture of an azo dye in this country. That was Aniline Yellow, introduced in 1863. But Aniline Yellow was no more than aminoazobenzene, obtained empirically by Griess in 1859. Yet even that was not the first azo compound. We must seek that in Perkin's primitive home laboratory in Shadwell. In that room, where Perkin first prepared his Mauve in 1856, and even before that discovery, Perkin and his fellow-student Church investigated the reduction of dinitronaphthalene. They isolated what we now call α-aminoazonaphthalene; to them it was "nitrosonaphthyline", later amended to "azodinaphthyldiamine". It was known to possess

dyeing power and was indisputably the first known azo compound.

When Griess moved to Burton, did he, one wonders, foresee the end of his diazo work? Or did Böttinger offer the prospect of enough leisure to make its continuance possible? We cannot be sure, but we might hazard a guess that some prospect was sought or offered. From all accounts the life of a brewery chemist was not at the time very exacting. Cornelius O'Sullivan, of Bass, Ratcliff & Gretton, complained that he was not fully occupied, and we read of Griess arriving punctually in his laboratory (Fig. 4) at 11.0 a.m. No, Griess was not at the end of his work— he had scarcely begun. One thing admits of no doubt, and that is the remarkable generosity of Allsopps to Griess. Griess spoke of "almost having to steal time" for his researches, but surely that was no more than a momentary twinge of self-pity quite foreign to his nature. It is far more likely that Allsopps were proud of him.

Griess uncovered most of the diazo reactions. He was familiar with the decomposition of diazo compounds into phenols and knew how to replace the diazo group by hydrogen. He prepared benzenediazonium nitrate and from it the crystalline sulphate, the platinichloride, aurichloride, ferricyanide, and nitrosoferricyanide, and the tin chloride double salt. He knew benzenediazonium perbromide and from it made the imide. He isolated benzenediazonium chromate in 1866, but it was his friend Caro who first thought of it as a potential military explosive. It was too dangerous to send away for test, so Caro carried it in his pocket by train to Sir Frederick Abel at Woolwich. It came to nothing, for the chromate was too unpredictable for safety.

In our own great world of colour, in which azo dyes outnumber those of any other class, we acknowledge our debt to Griess. The diazo reaction has given to chemists the most important single method yet known for producing soluble or insoluble coloured substances. Griess is commonly held to have discovered the coupling reaction in 1864. That, however, was the date when he first made it known. His letter to Watson Smith, to which reference has already been made, continues in this vein—

> Having obtained these diazo compounds I then tried their action upon all possible substances, amongst which, of course, are the numerous class of amido compounds. I found that the diazo compounds combine directly with these, forming frequently brilliantly coloured substances which dye directly animal fibres. The first colouring matter thus prepared by me, which I obtained in the years 1861–2, was benzene-azo-alpha-naphthylamine.

That dye is still in use today. About this time Griess prepared *p*-hydroxyazobenzene indirectly by treating diazobenzene with barium carbonate. At much the same time he discovered the first disazo dye, 2,4-bisphenylazophenol.

In 1863 Roberts, Dale & Co. placed on the market the first really successful azo dye, Martius's Bismarck Brown, although it was not made by a coupling reaction as we understand it. Yet Griess's work caused hardly more than a ripple in industry in those years. Industry was too preoccupied with Magenta and then with synthetic Alizarin. The first manufacture of an azo dye by Griess's method of diazotisation and coupling had to wait until 1876, when Otto Nikolaus Witt, working in the laboratory of Williams, Thomas & Dower at Brentford, discovered Chrysoidine. That was the beginning of a new phase of development. Roussin's famous oranges followed; then came, in 1878, Caro's Fast Red, often supposed to be the first red azo dye. It was, in fact, the first red azo dye which was commercially successful. The first red azo dye was Griess's β-naphtholazophenolsulphonic acid, dating from 1877. It was not until the eighties that azo dyes really came into their own. In part, this was due to the growing range of intermediates, but one of the greatest spurs to achievement was the discovery of the direct cotton dyes. The great landmark was Böttiger's patent of 1884 covering Congo Red, the first of the benzidine dyes with the power to dye cotton without the use of a mordant. How narrowly Griess missed that great innovation! Only two months before the publication of Böttiger's patent, Griess had covered the manufacture of similar dyes derived, not from benzidine, but from benzidinedisulphonic acid. His specification contained these momentous words: "The dyes which are produced by this invention mostly possess the valuable property of dyeing cotton goods without the use of mordants." Griess's dyes were technically valueless because they lacked affinity. Some say that this provides the most remarkable example of Griess's lack of technical perception. Others maintain that the criticism is unjust, because he was a brewing chemist and was never part of the dyemaking industry.

This was not Griess's first patent. That dates from several years earlier— from 1877. According to that specification, the amines derived from the reduction of nitrophenols, or substituted nitrophenols, were diazotised and coupled with phenols or naphthols. From this patent emerged the sole commercial colouring matter credited to Griess— Lancaster Yellow. Although manufactured by Storeys of Lancaster, it was not a success because of its high cost and lack of affinity. The patent was allowed to lapse, but more than twenty years later the dyes of this invention were discovered to be of value as chrome dyes, and the patent was a serious obstacle to the patenting of dyes of this type.

But this is no place for a catalogue of compounds and reactions. Griess published something like 140 papers in the leading scientific journals. How faint is our hope of doing him justice!

In 1869, when he was 40 years old, Griess married Louisa Anna Mason, the daughter of a well known Burton physician, and soon afterwards moved to a large house at Stapenhill on the outskirts of the town. That house stands today. During the 17 years of his married life, Griess watched the conquest of natural dyes by the science of man. He saw the madder trade extinguished almost overnight. He saw cochineal and fustic yield to man-made dyes steadily reinforced by azo dyes which

owed their beginning to him. By 1884 German patents alone covered more than 9,000 separate azo dyes. He watched the growth of great factories and the accumulation of wealth in which he had not the least share. He sought no reward, he looked for no honours, but when they came he was grateful and proud. He was elected to Fellowship of the Royal Society in 1869, and received an honorary doctorate from the University of Munich in 1877 (Fig. 5 and 6). From 1885 to 1887 he was vice-president of the Society of Chemical Industry. He was also vice-president of the Chemical Society, a committee member of the German Chemical Society, and a founder member of the Institute of Chemistry.

We now approach the last phase. By the early eighties the supremacy of the British coal-tar dye industry had declined alarmingly. Over 80% of the dyes used in this country were of foreign origin. Griess still felt the call of Germany. In 1883 he refused a tempting offer made by Caro—

> You can hardly imagine how difficult it is for me to turn down your offer, for nothing would be more to my liking than to work under your direction on a line for which I have had a special liking for so long. Unfortunately my domestic circumstances will not allow me this pleasure.

The domestic circumstances had to do with four children and a wife in failing health.

In the summer of 1888, a lonely saddened Griess, widowed for two years, travelled with his young children to Bournemouth for their annual holiday. On August 30th, at the age of 59, he died quietly and suddenly in his sleep. There is only one person living today who has first-hand knowledge of that tragic time—his daughter, Mrs. Mary Ard, now living in British Columbia. Last April Mrs. Ard's thoughts went back over the years and this is what she wrote—

> The day of my father's death is quite vivid in my mind, wondering in the morning why father had not been down to breakfast or appeared at all, and my sister saying to me "I believe he is dead" as though she had some intuition. Then later on our Uncle Philip suddenly appeared looking as he had never looked before, and we were frightened, and I think it was then that we were told the truth. I suppose under the unusual circumstances things had to be hurried up, for the next thing I remember was being taken to say good-bye to him as he lay in his coffin in the hall, and that was the end.

* * *

Mrs. M. Ard, daughter of Peter Griess, and Mrs. H. M. Griess, whose late husband was the younger of Griess's two sons, have most generously presented to Imperial Chemical Industries Ltd. Dyestuffs Division a small collection of letters, documents, and photographs formerly owned by Griess himself. The collection includes certificates of election to Fellowship of the Royal Society and to honorary membership of the Emperor Leopold-Charles Academy of Natural Philosophy at Halle, and the parchment of award of the honorary degree from the University of Munich (Fig. 5). Autograph letters from Griess to Adolf Baeyer (Fig. 6) and Charles Hermann Knoblauch, and the recipients' replies, are also present. There are several communications from the German Chemical Society bearing the signatures of Hofmann, Martius, Wichelhaus, Tiemann, and Liebermann. A selection of these historic documents was displayed during the Symposium.

The slides used to illustrate the lecture were prepared by Mr. L. G. Newman of ICI Dyestuffs Division. Those depicting Kirchhosbach, the house in which Griess was born (Fig. 2), and the University of Marburg were made from photographs provided by Dr. A. Wingler of Leverkusen-Bayerwerk, to whom acknowledgment is made for permission to use them. The author's thanks are extended also to Messrs. Ind Coope & Allsopp Ltd. for a picture of the brewery as it was in Griess's day, from which a slide was prepared, and for the modern photograph of Griess's laboratory (Fig. 4).

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Recent Work on the Mechanism of Diazotisation

J. H. RIDD

A reinvestigation of the kinetics of diazotisation, combined with a study of the exchange of ^{18}O between nitrous acid and water, has shown that the diazotisation of aniline in dilute mineral acids occurs by the interaction of the free amine with nitrous anhydride. The rate of formation of the nitrous anhydride can be the slow step of the reaction, and the reaction rate is then independent of the concentration of the amine. Other nitrosating agents (e.g. the nitrosonium ion) become important in more acidic solutions.

By discovering the diazotisation reaction, Peter Griess did more than open new pathways in the field of organic synthesis: he also presented later students of reaction mechanisms with a set of problems that are still not completely solved. This is not because the subject has been ignored: indeed, so much work has been published on the mechanism of diazotisation over the past sixty years that in one lecture it is possible only to pick out the main contributions that have led to our present concept of the processes involved*.

The main outlines of the reaction path by which a primary aromatic amine is converted into a diazonium salt have been clear since the early work of Hantzsch [1], and can be illustrated with reference to the analogous reactions of secondary amines.

* Fuller accounts of the history of this work will be found in references [1,7].

As is well known, these react with nitrous acid to give secondary nitrosamines. Primary amines would be expected to form primary nitrosamines in the same way, but Hantzsch showed that these are converted by a prototropic change into diazohydroxides; and diazo-hydroxides are known to ionise in acidic solutions to give diazonium ions. These reactions leading to the diazonium ion are shown below—

$$\mathrm{Ar{-}\overset{R}{N}{-}H \xrightarrow{HNO_2} Ar{-}\overset{R}{N}{-}N{=}O}$$

$$\mathrm{Ar{-}\overset{H}{N}{-}H \xrightarrow{HNO_2} Ar{-}\overset{H}{N}{-}N{=}O \rightarrow Ar{-}N{=}N{-}OH}$$

$$\rightleftharpoons \mathrm{Ar{-}\overset{+}{N}{\equiv}N + \overset{-}{O}H} \quad \text{(i)}$$

The initial nitrosation of the primary amine is usually rate-determining, and a kinetic study of diazotisation is then essentially a study of *N*-nitrosation.

The first kinetic study of diazotisation was that of Hantzsch and Schumann [2] in 1899. This work was concerned with the diazotisation, in dilute (0·002 M.) hydrochloric acid, of amines of a similar basicity to aniline, and the conclusions were that diazotisation was a second-order reaction and that, within experimental error, all the amines reacted at the same rate. The kinetics were expressed by equation (ii)—

$$\text{Rate} = k[\mathrm{Ar{\cdot}\overset{+}{N}H_3}]\,[\mathrm{HNO_2}] \quad \text{(ii)}$$

although the orders with respect to the individual reactants were not explicitly determined. Hantzsch assumed that, since there were two reactants, and since the kinetic order of the reaction was two, then the kinetics were first order with respect to each reactant. In writing the reactive form of the amine as the conjugate acid, Hantzsch was following the belief current at that time; the observed kinetic form would be equally consistent with a reaction of the free amine. Later workers, using a greater concentration of hydrochloric acid, supported Hantzsch's conclusions on the kinetic order of the reaction, but found marked differences in the rates of diazotisation of different amines.

The next major contribution to the subject was a detailed kinetic study of the diazotisation of aniline in sulphuric and hydrochloric acids carried out by Schmid [3] in 1936. He showed that the kinetics followed equation (iii) in concentrations of sulphuric acid of the order of 0·2 M.—

$$\text{Rate} = k\frac{[\mathrm{Ar{\cdot}\overset{+}{N}H_3}]\,[\mathrm{HNO_2}]^3}{[\mathrm{H^+}]} \quad \text{(iii)}$$

and that the same kinetic form could be observed in hydrochloric acid, but was then complicated by an additional term involving chloride ion catalysis. There are two differences between equation (iii) and equation (ii) that deserve comment. The inverse dependence of the reaction rate on the acidity, as shown in equation (iii), would have been missed by Hantzsch, because his experiments were carried out at an effectively constant acidity; this acidity dependence is now explained by postulating that it is the free amine and not the anilinium ion that takes part in the reaction. The dependence of the reaction rate on the square of the nitrous acid concentration in equation (iii) is in complete contrast to the earlier work, and for many years this inconsistency remained unexplained.

After 1936 some authors continued to discuss diazotisation in terms of equation (ii), considering that the second molecule of nitrous acid was in some way spurious. However, two suggestions were made to explain how the additional molecule of nitrous acid could appear in the kinetic expression, while being absent from the stoichiometric equation. Kenner [4] suggested the following series of reactions—

$$\mathrm{Ar{\cdot}NH_2 \xrightarrow[fast]{H_2ONO^+} Ar{\cdot}\overset{+}{N}H_2{\cdot}NO \xrightarrow[slow]{NO_2^-} Ar{\cdot}NH{\cdot}NO} \quad \text{(iv)}$$

The initial nitrosation is presumed to occur by the interaction of the free amine with a protonated nitrous acid molecule, and the nitrosoammonium ion so formed is considered to lose a proton to a nitrite ion and thus form the primary nitrosamine. Hammett [5] suggested that two molecules of nitrous acid first come together to form nitrous anhydride, and that this then reacts with the amine to form the primary nitrosamine—

$$2\mathrm{HNO_2} \rightleftharpoons \mathrm{N_2O_3 + H_2O}$$

$$\mathrm{Ar{\cdot}NH_2 \xrightarrow[slow]{N_2O_3} Ar{\cdot}\overset{+}{N}H_2{\cdot}NO \xrightarrow[fast]{} Ar{\cdot}NH{\cdot}NO} \quad \text{(v)}$$

This was the position in 1948, when work was started on this subject at University College London, under the guidance of Sir Christopher Ingold and Professor E. D. Hughes.

There is a possible experimental distinction between the two paths (iv) and (v) above, because, if the first step in (v) could be made rate-determining, the reaction rate would be independent of the amine concentration and dependent on the square of the nitrous acid concentration. This kinetic form is shown in equation (vi)—

$$\text{Rate} = k[\mathrm{HNO_2}]^2 \quad \text{(vi)}$$

In (iv) the amine is present in all stages, and a kinetic form of the type shown in (vi) is therefore impossible.

The kinetic form of the diazotisation of aniline was shown to fit equation (vi) in dilute (0·002 M.) solutions of perchloric acid, and this form should be the main term in the kinetic equation for diazotisation in a similar concentration of hydrochloric acid. As the acidity was increased, the kinetic form was observed to change to that of equation (iii), in agreement with the earlier work of Schmid in sulphuric acid media. The observed transition from (iii) to (vi) rules out the reaction path (iv), and it also reconciles the work of Hantzsch and Schumann with that of Schmid, for it satisfies Hantzsch's observation that the overall reaction order is 2 at low acidities. Hantzsch could not have distinguished between equation (vi) and equation (ii), since he worked only with equal concentrations of amine and nitrous acid, and the predictions of the two kinetic equations are then identical.

The simplest illustration of a zero-order reaction, as represented by equation (vi), is to use a large

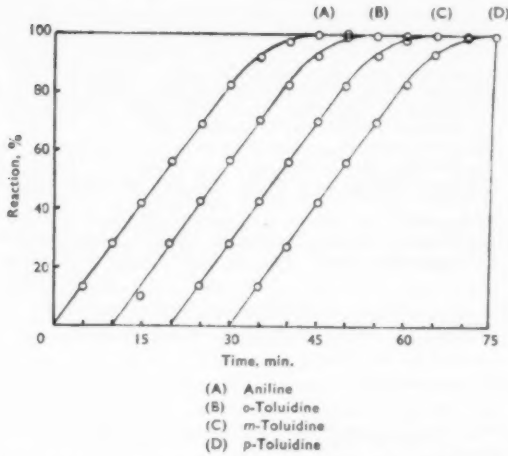


FIG. 1—Diazotisation of Amines at 0°C. with Nitrous Acid in Excess at pH 5 in a Phthalate Buffer. Initially $[Ar{\cdot}NH_2]ClO_4] = 0{\cdot}0005$ M., $[NaNO_2] = 0{\cdot}01$ M. The various amines are plotted for convenience as if started at 10-min. intervals.

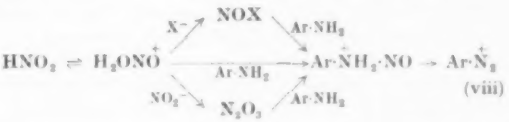
excess of the reactant determining the rate, and then to obtain a linear plot of the percentage reaction against the time. Such a plot is shown in Fig. 1 for the diazotisation of several amines in a buffer solution at pH 5. The instantaneous nitrous acid concentration is small, but it is maintained constant by the mobile acid–base equilibrium with the excess of sodium nitrite. The linear plots show that the reaction rate is independent of the concentration of the amine and also, over the range studied, of the nature of the amine. This latter observation is interesting confirmation of Hantzsch's earlier conclusion for diazotisation in feebly acidic solutions. These results, in conjunction with the kinetic form of equation (vi), strongly suggest that it is the rate of formation of nitrous anhydride which is being observed in these solutions.

If the amine is not present in the solution, the nitrous anhydride should be hydrolysed back to nitrous acid. Bunton and Stedman [6] at University College have obtained evidence on the rate of the back hydrolysis by studying the rate of exchange of oxygen atoms between nitrous acid and water, using water enriched in the ^{18}O isotope. The hydrolysis of the nitrous anhydride necessarily introduces an oxygen atom from the water into one molecule of nitrous acid, and so the rate of ^{18}O exchange between nitrous acid and water gives a maximum value* for the possible rate of formation and hydrolysis of nitrous anhydride—

$$2HNO_2 \longrightarrow N_2O_3 + H_2O$$
$$N_2O_3 + H_2{}^{18}O \longrightarrow HNO_2 + HNO^{18}O \qquad \text{(vii)}$$

The rate of oxygen exchange agrees well with the rate of diazotisation, and, more significantly, the kinetic form of the oxygen exchange [6] also fits equation (vi). These results show that oxygen exchange and diazotisation have a common intermediate formed from two molecules of nitrous acid in a process involving the breaking of one N–O bond. This almost proves that the intermediate concerned is nitrous anhydride.

Further investigations have shown that the apparent importance of nitrous anhydride in diazotisation is partly a consequence of the experimental conditions used in the early kinetic studies. Such conditions included amines of similar basicity to aniline and acid concentrations below 1·0 M. It is now known that the nitrous anhydride mechanism is only one of a family of reaction paths whose relative importance depends on the concentrations of the reactants, on the basicity of the amine, and on the acidity of the solution. Two other possible reaction paths, one involving the nitrous-acidium ion (H_2ONO^+) and the other involving the nitrosyl halides (NOX, X = Cl, Br, I), are shown below; they can both become effective in dilute solutions of mineral acids—



(viii)

There is not space to discuss in detail the characteristics of these other reaction paths, but the pattern shown in (viii) illustrates two significant points. Firstly, it can be seen that no reaction stage involves the attack of an amine or basic species on molecular nitrous acid: it appears necessary for nitrous acid to be protonated before it will react with the common nucleophilic reagents. The mechanism of the formation of nitrous anhydride is not known for certain, but since the above statement appears generally true, it is written in (viii) as an attack of a nitrite ion on a nitrous-acidium ion. Secondly, in dilute solutions of mineral acids there appears to be no observable nitrosation by the nitrosonium ion (NO^+). The distinction here between the nitrosonium ion and the nitrous-acidium ion may seem difficult because one is the hydrate of the other, but it can be settled by experiments based on oxygen exchange. Any formation of the nitrosonium ion in these solutions in sufficient concentration to affect the observed rate of diazotisation would give rise to an additional term in the kinetic equation for the exchange of ^{18}O between nitrous acid and water, and this term is not found.

The results described above have already been published [7], but work is continuing on other aspects of diazotisation, with particular reference to diazotisation in strongly acidic media (~60% H_2SO_4 and 60% $HClO_4$). Spectroscopic studies [8] in such media show that the nitrous acid is not present as the molecular species HNO_2 but as ionised nitrosonium salts (e.g. $NO^+HSO_4^-$). The nitrosonium ion would be expected to be the most powerful nitrosating agent, in the same way as the nitronium ion is the most powerful nitrating agent, and so, where the nitrosonium ion is the main nitrous species present, it should also be the effective agent in the nitrosation of the amine.

* A maximum value because, in principle, exchange could occur by other mechanisms besides the formation of nitrous anhydride.

The kinetic studies on the diazotisation of aniline support this view: thus the order with respect to nitrous acid falls from the value 2 in dilute sulphuric acid (characteristic of nitrosation by nitrous anhydride) to the value 1 in 60% sulphuric acid (consistent with nitrosation by the nitrosonium ion). Nevertheless, certain problems remain, associated with the variation of the reaction rate with acidity, and it is possible that proton transfers may become partly rate-determining.

The effect of the basicity of the amine on the mechanism of diazotisation has been studied by Larkworthy. The preliminary nitrosation stage of the diazotisation reaction consists of an attack by the nitrosonium ion or by a carrier of the nitrosonium ion (e.g. N_2O_3) on the unshared electron pair at the nitrogen atom of the free amine. The presence of electron-attracting substituents in an aniline derivative would therefore be expected to decrease the reaction rate, and the less basic amines would be expected to require the more reactive nitrosating agents. These predictions are found to be true, but in assessing the effect of a substituent on the reaction rate, it is necessary to take account of the change in the acid–base equilibria involved: under some conditions, the introduction of an electron-attracting substituent can increase the observed reaction rate by increasing the concentration of free amine in the solution.

The catalytic effect of strong acids on the diazotisation of the weakly basic amines appears to arise partly because of a solubility effect, but mainly because the concentrations of the more reactive nitrosating agents (H_2ONO^+, NO^+) increase greatly with acidity. The fact that the increase in acidity also increases the protonation of the amine is incidental, and should in itself decrease the reaction rate; the old theory that the conjugate acid of the amine takes part in the reaction receives no support from the detailed kinetic studies.

Our present knowledge of the mechanism of diazotisation can be summarised as follows. The reaction involves the formation and rearrangement of a primary nitrosamine. At low acidities there are a number of ways by which this nitrosamine can be formed: nitrosation with nitrous anhydride is particularly important with amines of basicity similar to that of aniline, but nitrosation by the nitrous-acidium ion is more important with amines of basicity similar to that of *p*-nitroaniline. At high acidities, the nitrosation presumably occurs by the interaction of the amine and the nitrosonium ion, but these reactions are not yet perfectly understood.

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(*MS. received 3rd November 1958*)

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Discussion

Professor W. BRADLEY: The lecturer has referred to the important part played by N_2O_3 in the diazotisation process in weakly acid solution and has given quantitative expressions in support. Does this mean that N_2O_3 is not lost by dissociation—

$$N_2O_3 \rightarrow NO + NO_2 \rightarrow \text{Further products?}$$

Dr. RIDD: I have no doubt that the N_2O_3 would dissociate in the way that Professor Bradley has suggested if it had time to do so. However, under the conditions of equation (vi) the N_2O_3 is apparently reacting rapidly with the amine, so rapidly that no appreciable fraction of the N_2O_3 has time to react with the water that surrounds it. Under such conditions it seems reasonable to suppose that the N_2O_3 does not have time to undergo homolytic dissociation. This presumably applies also to the more acidic conditions studied by Schmid[3].

Professor BRADLEY: The lecturer has shown that in more strongly acid solution the ion NO^+ is formed, which then attacks the amino group of primary amines. However, aniline undergoes substitution in the nucleus with very great ease with a wide variety of agents such as bromine, aldehydes, and nitroso compounds. For this reason it is very interesting that in diazotisation no nuclear substitution is commonly found, but only a reaction with the amino group. Why does this difference arise?

Dr. RIDD: I cannot offer a complete explanation of this difference, but it may be helpful to draw an analogy with protonation. The addition of an NO^+ ion to aniline may be similar to the addition of a proton, and there is no doubt that, in the free amine, this process occurs more readily at the nitrogen atom than at a carbon atom of the ring. Nitrosation at one of these carbon atoms should occur readily, but if its speed is only 1% of that of diazotisation, it would not be easy to detect. After diazotisation has occurred, the aromatic ring is deactivated to further attack. Nevertheless, as Blangey[9] showed some time ago, *C*-nitrosation can compete with *N*-nitrosation and diazotisation at very high acidities, and we hope to investigate this subject in our study of diazotisation in strong sulphuric acid.

Mr. A. S. FERN: The previous discussion about diazotisation under highly acidic conditions, where the concentration of water is relatively low, is interesting in connection with diazotisation inside such hydrophobic fibres as polyamides and

polyesters. Can the concentration of water in a diazotisation system determine the rate of reaction?

Dr. RIDD: I think that the main chemical function of water in an aqueous diazotisation is to accept a proton from the protonated primary nitrosamine formed in the initial nitrosation step. Since the nitrosation stage is usually rate-determining, the latter stage involving the water should have no influence on the reaction rate. However, we have some evidence that, in 60% sulphuric acid, the proton transfers can be relatively slow, and may then have some influence on the reaction rate. This could, perhaps, apply also to diazotisation inside a fibre. It would be interesting to study the kinetics of diazotisation in some non-aqueous solvents at low acidity.

Mr. R. K. FOURNESS: I hope that Dr. Ridd intends to extend his valuable studies to systems where the acid concentration exceeds 60% sulphuric acid, because such systems are being more widely used in azo dye synthesis as the demand for the use of amines of greater complexity increases.

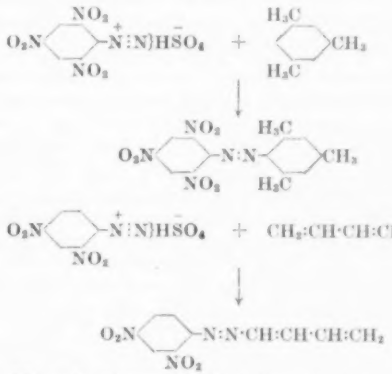
Dr. RIDD: We intend to continue this work into as high an acidity as possible. With amines of the basicity of aniline, we then expect to find that *C*-nitrosation will compete with diazotisation.

The Mechanism of the Coupling Process

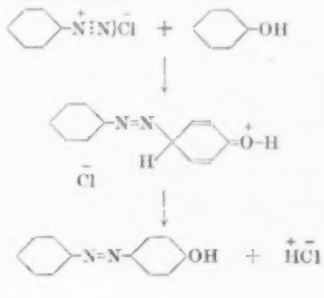
W. BRADLEY

The development of modern views of the mechanism of the coupling process is reviewed.

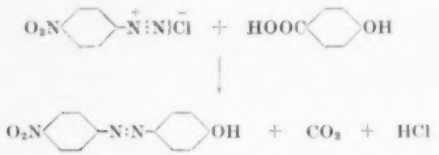
Although a few hydroxyazo and aminoazo compounds were found at about the same time as Peter Griess discovered the diazotisation reaction, the first clear example of the coupling reaction was not described until a few years later [1]. Appropriately, Griess again was the discoverer, and the particular example which he described was the interaction of benzenediazonium nitrate and α-naphthylamine to form 4-phenylazo-1-naphthylamine. Important though this observation proved to be, it caused no stir at the time. Even its extension to the reaction of diazotised amines with phenols did not occur until 1870, when Kekulé and Hidegh [2] found that benzenediazonium chloride and phenol gave *p*-hydroxyazobenzene. When it was found that sulphonated compounds could be used and that the products were of value commercially, interest in the coupling reaction became intense, and many hundreds of amino- and hydroxy-azo compounds came to be made and studied. Several theoretical schemes were put forward to explain the course of the coupling reaction, but none of these had permanent value, and it was not until 1920 that we can discern the seeds from which modern views have grown. On the practical side, on the contrary, important discoveries were being made. First it was found that the coupling reaction was applicable to a wide range of phenols and amines in the benzene and naphthalene series. Later it transpired that heterocyclic phenols, such as methylphenylpyrazolone, could be used, and even derivatives of acetoacetic acid [3]. In the early years of this century it was shown, for example, that useful pigments could be prepared by coupling selected diazotised amines with various acetoacetarylides [4]. It thus became clear that the presence of an aromatic nucleus was not essential for coupling to take place, and in 1912 and 1919 K. H. Meyer showed that even hydroxyl and amino groups could be dispensed with when a sufficiently reactive diazotised amine was used. Thus diazotised picramide and 2,4-dinitroaniline could be coupled even with hydrocarbons such as mesitylene and 1,3-butadiene—



Meyer's discovery that diazotised amines could be coupled with butadiene led to the idea that coupling is essentially the result of the attack of a diazotised amine on a carbon atom in the second component, and Lapworth showed that coupling occurs because the second component is able to provide electrons to bind diazonium ions. Robinson, who worked closely with Lapworth in the study of the chemical reactivity of organic compounds, published on several occasions pictorial representations of this aspect of the coupling process. Robinson contributed also the idea that in the coupling of phenols and aromatic amines the hydroxyl and amino groups assist the coupling reaction by allowing their own electrons to participate in the total reaction—

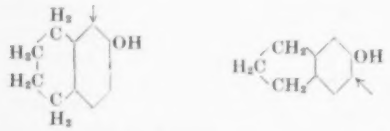


Robinson's scheme enabled a simple explanation to be given of the occurrence of coupling even when the normal coupling position was occupied by a substituent such as carboxyl, the substituent being eliminated during the reaction. A familiar example is the reaction of diazotised *p*-nitroaniline with *p*-hydroxybenzoic acid, 4-hydroxy-4′-nitroazobenzene being formed with elimination of the carboxyl group—



It accounted also for the demethylation of aryl methyl ethers which had been observed during coupling. In 1930 Mason and Jambuserwala found that several diazotised amines on being coupled with 2,3-methoxynaphthoic acid gave mixtures of 1-arylazo-2-methoxy-3-naphthoic acids and 1-arylazo-2-hydroxy-3-naphthoic acids, partial demethylation having occurred.

Many unexpected orientation effects have been observed in the coupling of phenols and amines, and generally the explanation is that electrons are most readily available at the point where coupling occurs. Thus *β*-naphthol couples only in the 1-position, though 3-, where no coupling occurs, is also an *ortho* position. 4-Hydroxypyrene couples with diazonium salts whereas 3-hydroxypyrene does not, though again an *ortho* position is free. Mills and Nixon showed in 1930 that, whereas 5,6,7,8-tetrahydro-*β*-naphthol coupled in the 1-position, 6-hydroxyhydrindane gave the 5-arylazo derivative—



And in general the introduction of such electron-attracting groups as Cl, NO_2, SO_3H into a phenol or an amine diminishes its ability to couple with diazotised amines.

The part played by the diazotised amine has proved difficult to assess. This is because the equilibrium—

Diazonium ion ⇌ Diazo-hydroxide ⇌ Diazoate anion

occurs and can be demonstrated in aqueous solution.

Recent work has shown beyond doubt that in aqueous solution it is the diazonium ion which is the effective agent. This has been elegantly demonstrated by H. Zollinger, who diazotised *p*-toluidine, sulphanilic acid, and aniline-2,5-disulphonic acid and coupled the resulting diazotised amines with 2-naphthylamine-6-sulphonic acid in the presence of sodium acetate. Each coupling was done a number of times in the presence of increasing concentrations of potassium chloride. With diazotised *p*-toluidine the coupling rate fell with increase in the concentration of potassium chloride; with sulphanilic acid there was no effect; and with aniline-2,5-disulphonic acid the rate was increased. On Bronsted's interpretation of salt effects in bimolecular ionic reactions the results point clearly to the diazonium forms as the essential active species in the coupling reaction with all three amines.

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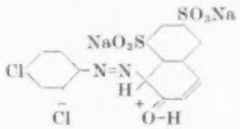

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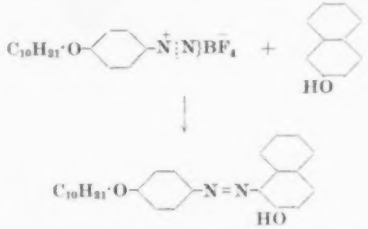

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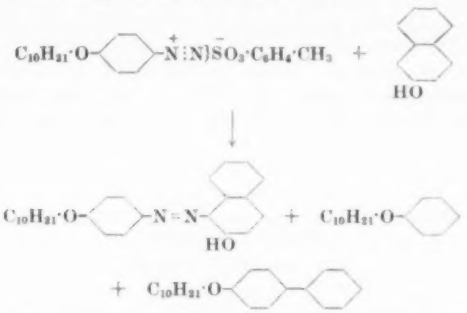

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References

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AFTERNOON SESSION

Chairman—Mr. CLIFFORD PAINE (*Immediate Past President*)

Relative Rates of Reduction of a Series of Azo Compounds

G. P. WARWICK*

The chemistry and the pharmacology of the nitrogen "mustards" are briefly summarised, and the importance of azo compounds in cancer research is indicated. The concept of "latent activity" is introduced, and special attention is devoted to the *p*-phenylazo derivatives of *NN*-bischloroethylaniline as examples of such compounds used in the chemotherapy of cancer.

The literature concerning the rates of reduction of azo compounds is briefly reviewed. The rates of reduction of some derivatives of 4-*NN*-bis-2″-chloroethylamino-azobenzene with stannous chloride, hydrazine, and the xanthine–xanthine oxidase system are discussed in relation to the electronic character of ring substituents; attention is drawn to certain anomalous "*ortho*" effects. The rates of reduction are discussed also in relation to the observed tumour-growth-inhibiting properties of the compounds.

Few would disagree with the statement that azo compounds are among the most interesting chemicals with which a scientist can work. In the past, interest in them centred on their chemical and physical properties, viz. their ability to act as dyes, their spectra, and their stereochemistry. During more recent years, however, more and more attention has been focused on their biological properties, which are at once diverse and of fundamental importance. Although the rates of reduction of substituted azo compounds with various agents would appear to be a purely chemical problem, it might be of interest to introduce into the paper a more biological flavour.

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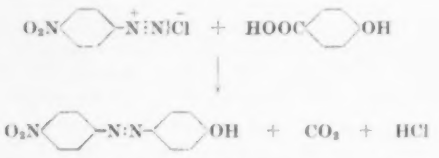
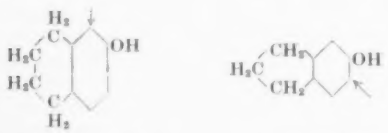
Robinson's scheme enabled a simple explanation to be given of the occurrence of coupling even when the normal coupling position was occupied by a substituent such as carboxyl, the substituent being eliminated during the reaction. A familiar example is the reaction of diazotised *p*-nitroaniline with *p*-hydroxybenzoic acid, 4-hydroxy-4′-nitroazobenzene being formed with elimination of the carboxyl group—



It accounted also for the demethylation of aryl methyl ethers which had been observed during coupling. In 1930 Mason and Jambuserwala found that several diazotised amines on being coupled with 2,3-methoxynaphthoic acid gave mixtures of 1-arylazo-2-methoxy-3-naphthoic acids and 1-arylazo-2-hydroxy-3-naphthoic acids, partial demethylation having occurred.

Many unexpected orientation effects have been observed in the coupling of phenols and amines, and generally the explanation is that electrons are most readily available at the point where coupling occurs. Thus *β*-naphthol couples only in the 1-position, though 3-, where no coupling occurs, is also an *ortho* position. 4-Hydroxypyrene couples with diazonium salts whereas 3-hydroxypyrene does not, though again an *ortho* position is free. Mills and Nixon showed in 1930 that, whereas 5,6,7,8-tetrahydro-*β*-naphthol coupled in the 1-position, 6-hydroxyhydrindane gave the 5-arylazo derivative—



And in general the introduction of such electron-attracting groups as Cl, NO_2, SO_3H into a phenol or an amine diminishes its ability to couple with diazotised amines.

The part played by the diazotised amine has proved difficult to assess. This is because the equilibrium—

Diazonium ion ⇌ Diazo-hydroxide ⇌ Diazoate anion

occurs and can be demonstrated in aqueous solution.

Recent work has shown beyond doubt that in aqueous solution it is the diazonium ion which is the effective agent. This has been elegantly demonstrated by H. Zollinger, who diazotised *p*-toluidine, sulphanilic acid, and aniline-2,5-disulphonic acid and coupled the resulting diazotised amines with 2-naphthylamine-6-sulphonic acid in the presence of sodium acetate. Each coupling was done a number of times in the presence of increasing concentrations of potassium chloride. With diazotised *p*-toluidine the coupling rate fell with increase in the concentration of potassium chloride; with sulphanilic acid there was no effect; and with aniline-2,5-disulphonic acid the rate was increased. On Brønsted's interpretation of salt effects in bimolecular ionic reactions the results point clearly to the diazonium forms as the essential active species in the coupling reaction with all three amines.

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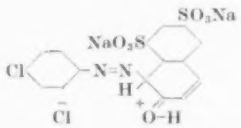

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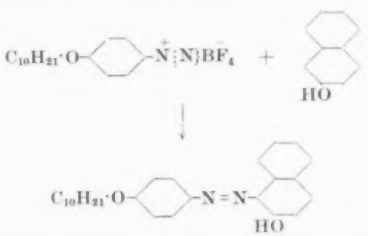

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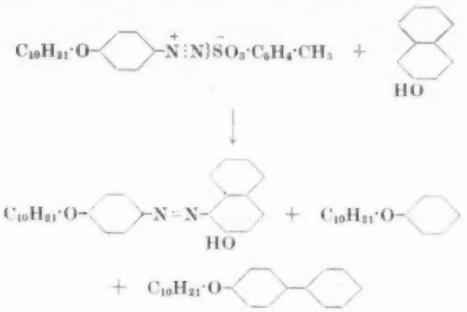

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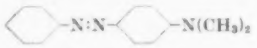
Firstly, therefore, our reasons for making these particular azo compounds, and the place of azo compounds in general in cancer research, will be considered.

For a number of years those who work in the field of cancer have been interested in azo compounds. The reason for this interest is manifold and springs from our knowledge that certain classes of azo compound can manifest interesting biological and pharmacological effects in the animal body—properties which have supplied us with invaluable information. Thus it has been known for many years that dimethylaminoazobenzene—



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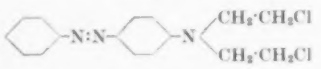
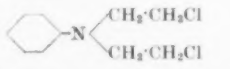
better known as "Butter Yellow", and certain of its derivatives are very specific in their ability to cause liver cancer in rats [1]. By studying the liver during the precancerous stages, the effect of dietary changes on the carcinogenicity of the azo dye, and the metabolism of the azo dye itself, including its ability to form strong complexes with liver protein, we are getting ever nearer the goal of understanding the mechanism of this carcinogenic process.

More recently, Professor A. Haddow (*personal communication*) has found that certain derivatives of azobenzene are able to inhibit the growth of animal tumours, and Dr. L. A. Elson (*personal communication*) has shown that they are active against certain of the blood components. The simplest member of this series is an azobenzene bearing a nitrogen "mustard" group in the *para* position to the azo linkage—



(II)

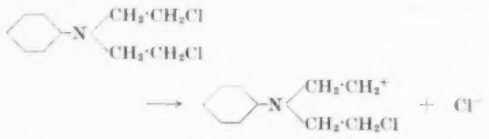
For many years we have been interested in bis-2-chloroethylaniline—



(III)

and its derivatives, because these compounds are able to inhibit cell division and are therefore potentially useful in the chemotherapy of certain forms of cancer and blood disorders such as leukaemia. However, these compounds are unfortunately not specific in their effects on tumour-cells and actually attack all cells, whether normal or malignant, which are undergoing division. The result is that they attack the bone marrow and the gastro-intestinal tract with resulting high toxicity to the host; they attack also the central nervous system and the parasympathetic nervous system, causing distressing symptoms such as nausea and dizziness. It has been the aim of chemists at the Chester Beatty Cancer Research Institute to synthesise "mustards" which, while being highly toxic to the tumour cell, are relatively without effect on normal tissue. This is a difficult task, because tumour cells are qualitatively identical to normal cells in most respects.

The nitrogen "mustards" are normally very reactive chemically and function as electrophilic reagents. In aqueous media they first form a carbonium ion—



which is capable of reaction with electron-rich centres such as those present in protein or nucleic acid [2]. It is by such reactions that these compounds are thought to elicit their biological effects. Since the reaction is of the S_N1 type, electron-releasing ring substituents will facilitate reaction, while electron-attracting ring substituents will retard reaction. It has, in fact, been shown that inhibition of tumour-growth does not occur unless the chlorine atoms have a certain level of chemical reactivity (cf. Table I) [3].

TABLE I

Chemical Reactivity and Biological Activity of Phenyl "Mustards"

$R\text{-}C_6H_4\text{-}N(CH_2\text{-}CH_2Cl)_2$

R	Hydrolysis (%)*	Biological Activity†
4-NH_2	100	+
2-CH_3-O	89	+
2-CH_3	83	+
4-CH_3-O	58	+
4-CH_3-CO-NH	41	+
4-CH_3	38	+
3-CH_3	21	+
H	20	+
4-C_6H_5	12	−
4-Cl	9	−
4-C_2H_5-O-CO	<1	−
4-CHO	<1	−
2,4-di-NO_2	<1	−
4-NH_2-CO	<1	−

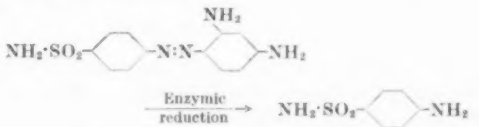
* In 50% acetone at 66°C. for 30 min.

† As measured by ability to inhibit the growth of the transplanted Walker rat-carcinoma 256.

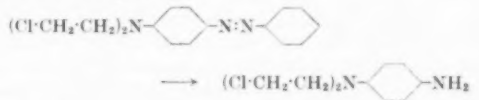
Since the "mustards" attack not only tumour cells but also all other rapidly dividing cells in the body, obviously the distribution of the drug within the host will be important. If we could synthesise a drug which would concentrate preferentially in the tumour, then our goal would be well in sight. With this ideal end in view, "mustards" have been synthesised containing various solubilising ring substituents, with some modest success [4, 5]. Another approach has been to synthesise a "mustard" possessing a low chemical reactivity and hence devoid of ability to interfere with tumour growth, but capable of some change *in vivo* which would activate it chemically and enable it then to exert its biological effect of tumour-growth-inhibition [6]. Using this approach, we could vary not only the solubility and hence the distribution of the drug *in vivo*, but also the actual site at which reactive "mustard" would be released, since we hoped that the transformation of chemically

unreactive molecule to chemically reactive molecule might not take place equally well at all sites in the body. By this we hoped to achieve some lowering of general toxicity without loss of tumour-growth-inhibition. The derivative chosen was the azo compound mentioned earlier (II).

The *p*-phenylazo linkage is powerfully electron-attracting, with the result that the "mustard" chlorine atoms will be unreactive and the molecule will be unable to undergo the typical reactions of "mustards" with anions. Consequently it was considered that the compounds as such would be incapable of tumour-growth-inhibition. However, in the work done on Prontosil which led to the discovery of sulphanilamide [7], the azo compound itself was inactive against the micro-organism, and it was only after reduction in the host that inhibition occurred—



In an analogous manner the azo "mustard", itself inert, could give rise to the amine, which is a highly reactive cytotoxic compound and if liberated within a tumour cell would almost certainly interfere with its growth—



When tested against an experimental tumour by Professor Haddow this was certainly shown to be the case.

Encouraged by this initial success, we decided to synthesise and examine a large number of derivatives of this type, some bearing substituents in one ring and some in both rings [8]. The effect of substituents was quite remarkable in that sometimes activity was greatly enhanced and sometimes it was diminished or removed entirely. Since we felt that biological activity depended on reduction of the azo linkage *in vivo*, it was tempting to think that the effect of substituents was either to increase or to decrease the ease of reduction and so increase or decrease biological activity. We decided to test this hypothesis by actually measuring some rates of reduction *in vitro* to see whether any correlation could be found between ease of reduction and ability of the compound to stop tumour-growth [9, 10].

Although many agents are known which can reduce azo compounds, very little has been published about the kinetics of the reactions. Thus, for example, very little work has been done on the polarographic reduction of azo compounds, and indeed, the problem of interpreting the experimental waves appears to be very complex, resulting in the appearance of some conflicting statements in the literature. The polarographic reduction of each azo compound appears to present a considerable problem in itself, and our hopes of comparing the reduction potentials of a large number of azo compounds by this method appeared very slight. It is worth mentioning in passing that some very interesting data have arisen from the polarographic reduction of azo compounds [11]. Thus, for instance, Vladimerstev and Postovskiĭ reported half-wave potentials for a series of azobenzenes (Table II). It is seen that electron-releasing ring substituents increase the resistance of the azo linkage to reduction, as would be expected from the electronegativity rule propounded earlier by Shikata and Tachi [12].

TABLE II

Half-wave Potentials of a Series of Azobenzenes

$R{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_5$

R	Half-wave Potential (mv.)
H	−320
4-HO	−383
4-$CH_3{\cdot}O$	−358
4-$CH_3{\cdot}COO$	−322

Another method which has been used to study the relative reduction rates of azo compounds is catalytic reduction, developed by Hamon and co-workers in their study of Prontosil-like compounds. In her comprehensive article [13] some of the inherent difficulties of the technique are indicated. The main difficulty apparently lies in standardising the experimental conditions. It is obvious that factors such as quantity and activity of catalyst, speed of shaking, temperature, and so on are all variables which will influence the rate of hydrogenation and many of which are difficult to control. However, Hamon did conclude that azo compounds bearing a substituent *ortho* to the azo linkage are normally reduced more rapidly than those bearing substituents in the *meta* and *para* positions.

Some information correlating structure with ease of reduction was presented by Tréfouël and co-workers [14], who observed the relative rates of reduction of several azo compounds using cysteine at 95°c. They showed that Prontosil was reduced very rapidly to the amines under these conditions, while Congo Red (C.I. 2086), Trypan Blue (C.I. 23850), and Afridol Violet were reduced much more slowly. However, cysteine was found not to be a suitable reducing agent for the azo "mustards", partly because of the sluggishness of the reductions and also because in some instances cysteine is able to react with the "mustard" grouping.

TABLE III

Rates of Reduction of Azo Compounds with Live Yeast [15]

$R{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2$

R	Reduction Time (hr.)
H	20
2-OH	> 100
4-OH	20
2,4-di-OH	70
2-COOH*	0·5
4-COOH	3·5

* Methyl Red (C.I. 13020)

Recently Mecke and Schmähl [15] have developed a spectroscopic method for comparing the relative reduction rates of a series of azo compounds using live yeast, and their results are shown in Table III. This accelerating effect of an *ortho* carboxyl substituent is very relevant to our own studies. However, reductions normally proceeded relatively slowly, and the method was not really satisfactory for our purposes.

Ideally we wanted a reducing agent which would be stable and would function rapidly at pH 7. We tried many reducing agents buffered at pH 7, including sodium hydrosulphite, thiourea dioxide, and sodium formaldehyde-sulphoxylate, but without success. All these reagents are very useful when one simply wishes to carry out a reduction on a preparative scale, but they are useless for rate measurements owing to their instability in aqueous solution. Thus solutions of these reagents even in the absence of oxygen rapidly decomposed to strongly acidic products, and no buffer was able to hold the pH of the medium constant. We were finally left with the choice of using either titanous chloride, a reagent used earlier in acid solution by Hinshelwood [16, 17], or stannous chloride also in acid solution. We chose the latter, but were painfully aware of the very "unbiological" pH at which reduction measurements would have to be carried out, and we did not feel particularly hopeful that any correlation with ease of reducibility *in vivo* would be forthcoming. Stannous chloride in ethanolic hydrochloric acid was found to maintain its titre for several days when stored under nitrogen, and was stable during reduction-rate measurements, for which a spectroscopic method was developed.

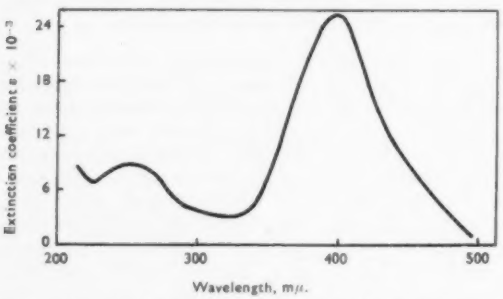
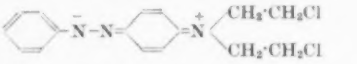


FIG. 1—Absorption Spectrum of 4-Bis(2-chloroethyl)aminoazobenzene in 95% Ethanol

In neutral solution almost all the azo compounds in this series showed their main absorption peak at about 4000 A.[18], and in Fig. 1 is shown the spectrum of the unsubstituted azo "mustard" in ethanol. When the azo compounds are treated with acid, this main peak at 4000 A. undergoes a bathochromic shift of some 1300 A. to 5300 A., as a result of the presence of a new species in solution, viz. the monoprotonated form. In a molecule such as II the first proton could conceivably add to any of the three nitrogen atoms, and with compounds such as dimethylaminoazobenzene (I) a controversy has raged for years as to where the proton adds. Without entering into great detail on this point, our conclusion is that in the azo "mustards" the first proton adds on to the azo nitrogen farthest from the "mustard" group. Such addition is facilitated by an electromeric displacement of electrons from the "mustard" nitrogen (IV)—

(IV)

giving rise to the extreme form (V)—



(V)

one of the main contributors to the resonance hybrid of the protonated form being VI—

(VI)

which is thought to be mainly responsible for the deepening in colour observed when these compounds are treated with acid.

Ring substituents, such as *p*-methoxyl and methyl, which release electrons into the azo linkage increase the proportion of the quinonoid form at any particular acidity, while electron-attracting substituents such as nitro and the halogens inhibit proton addition, and some of these compounds do not undergo a change in spectrum even in fairly strongly acid solution. Hence the spectra of all the azo compounds examined were measured in ethanol and then in ethanol containing hydrochloric acid, the peak of greatest intensity in the acid medium being the one observed during measurement of the reduction rate. Thus the solution of unsubstituted compound (II) contained about equal proportions of protonated and non-protonated forms at the acidity used, while the *p*-nitro derivative was still almost completely in the azo, unprotonated form, and the change in intensity of this peak was observed during the measurement of the rate of reduction of this compound. As an azo compound underwent reduction each peak diminished in intensity, and by taking measurements of light absorption at various intervals of time the rate of reduction could be calculated.

Since a large excess of stannous chloride was used, the reductions followed pseudo-unimolecular kinetics. All rates were measured relative to that of the unsubstituted compound, and as a precaution the rate of reduction of this compound was always measured alongside the compound under examination. Its rate of reduction varied little from day to day, mainly because of the stability of the stannous chloride solution and because the Unicam spectrophotometer was well thermostated at 23°C. In most cases reductions were virtually complete after 15 min. The rate constant for the unsubstituted compound was k_0, so the relative rate of reduction of the test substance was k/k_0, which was arbitrarily multiplied by 100.

As will be seen from Table IV, some substituents increased the rate of reduction, while others

TABLE IV

Rates of Reduction by Stannous Chloride

Substituent	Relative Rate Constant $\left(\frac{k}{k_0} \times 100\right)$
None	100
2-CH_3	Very low
2′-CH_3	62
3′-CH_3	94
4′-CH_3	36
2′-C_6H_5	68
4′-C_6H_5	101
2-CH_3·O	152
3′-CH_3·O	204
4′-CH_3·O	20
2′-Cl	113
3′-Cl	278
4′-Cl	206
2′-Br	80
3′-Br	297
4′-Br	254
2′-I	39
4′-CH_3·CO	2100
2′-$COOCH_3$	Very high
2′-COOH	Very high
3′-COOH	166
4′-COOH	1180
2′-NO_2	>1500
2′-SO_3H	2470
4′-SO_3H	374
2′,3′-Cl_2	90
2′,4′-Cl_2	75
3′,4′-Cl_2	417
2-CH_3, 2′-COOH	562
2-CH_3·O, 2′-COOH	91
2-CH_3, 4′-CH_3, 2′-COOH	168
2-CH_3, 4′-COOH	93

decreased it, and it might be of interest to analyse these results further. Thus electron-releasing substituents hindered reduction, while electron-attracting substituents enhanced it, and in some cases we found an outstanding *ortho* effect.

We may examine more closely the effect of 3′ and 4′ substituents. A chlorine atom in the 4′ position, for example, is able to attract electrons by an inductive effect, but has a tendency to release them by a mesomeric transfer; a chlorine atom in the 3′ position also can attract electrons by an inductive mechanism, but it has no tendency to release them, since mesomerism from this position is impossible. Thus a 3′-chlorine atom has a greater tendency to attract electrons than a 4′-chlorine atom, and it is not surprising, therefore, that the 3′-chloro compound is more rapidly reduced than the 4′-chloro compound Similarly, a 4′-methoxyl group has a great tendency to release electrons into the azo linkage, and hence the 4′-methoxy derivative has a very low rate of reduction; when in the 3′ position, however, the methoxyl group is able to exert its electron-attracting inductive effect, and hence clearly raises the rate of reduction. Similarly, a 4′-methyl group is able to release more electrons into the azo linkage than a 3′-methyl group, for in the former case we have not only inductive release but also the possibility of hyperconjugation (the Baker–Nathan effect). In view of this apparent relation between electron density of the azo linkage and ease of reduction, we plotted Hammett's σ values [19] against the logarithm of the relative rate constant, and obtained a reasonably good straight line (Fig. 2). From the equation log—

$$\log k - \log k_0 = \sigma\rho$$

we were able to calculate a value of 1·59 for ρ, i.e. the slope of the Hammett curve.

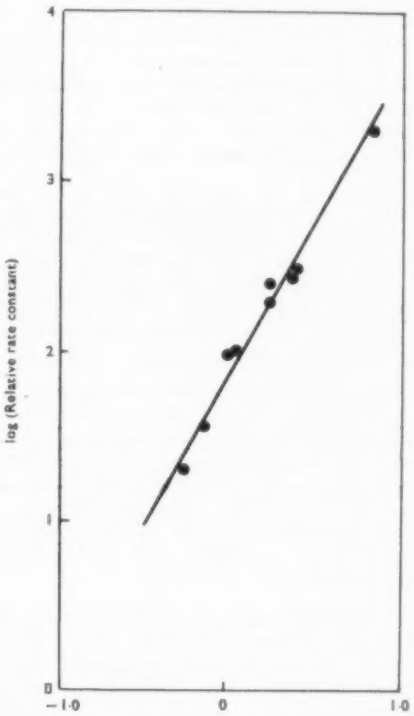


FIG. 2—Logarithmic Plot of Relative Rate Constant for Reduction with Stannous Chloride against Hammett's σ Constant

While the *m′* and *p′* substituents behaved in this way, substituents in the two positions *ortho* to the azo linkage obviously caused steric effects. For example, the relative rates of reduction of the three halogen derivatives—2′-chloro, 2′-bromo, and 2′-iodo—were 113, 80, and 39. Without considering electronic effects, it seems fairly certain that the decreasing rate of reduction caused by these substituents is due to a primary steric effect

increasing with increasing bulk of the atom. This was also the case with the 2′-phenyl substituent, for while a phenyl substituent in the 4′ position had virtually no effect on the rate of reduction (101), when in the 2′ position it caused almost a 50% drop in the rate.

Possibly the most interesting *ortho* effect was that associated with the 2′-carboxylic acid. This compound was reduced so rapidly that no measurement could be made of its rate of reduction. After detailed examination of its ultraviolet and infrared absorption* spectra[18] we concluded that the unionised form exists as a hydrogen-bonded hybrid. This compound also possesses a powerful ability to chelate with metal ions, and it is quite likely that in stannous chloride solution a chelated species may be formed. By having the stannous ion actually associated with the azo linkage in this way an enhancement of the transfer of electrons in the oxidation–reduction reaction could be envisaged.

The reduction of the 2′-nitro derivative was of interest, for in this case it was theoretically possible that both the nitro group and the azo linkage could undergo reduction simultaneously. What actually occurred was that the azo linkage was very rapidly reduced, yielding 100% of *o*-nitroaniline, which seemed quite stable under these conditions.

Summarising, we may say that in the case of *m*′- and *p*′-substituted compounds rates of reduction with stannous chloride were in the order which would be anticipated if the rate-determining step were electron addition to the azo linkage followed by rapid proton addition. *ortho* Substituents behaved anomalously, sometimes decreasing, sometimes increasing, reduction rate.

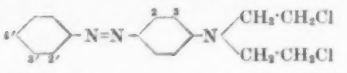
These results were possibly of interest from a purely chemical point of view, but we were still far from achieving our goal of determining a correlation or otherwise between the ease of reduction of these compounds *in vitro* and their ability to stop the division of cancer cells. It is not surprising that such a correlation was not obtained under the extremely acid conditions used in the stannous chloride reductions.

As mentioned earlier, we had unsuccessfully tried several reducing agents at pH 7. We continued our search, however, and eventually were rewarded by finding that hydrazine at pH 8 was stable when stored in an atmosphere of nitrogen, and reduced most of the azo compounds at a satisfactory rate. When the dihydrochloride was three-quarters neutralised, the pH of the solution was about 8, and this solution acted as its own buffer. In this case none of the azo compounds was in the protonated form, and so the peaks at 4000 A. were used for the reduction runs. In view of the extreme lack of reactivity of the chlorine atoms in the azo compounds, it was considered that, under the conditions employed, reaction of hydrazine with the "mustard" group would not proceed to any appreciable extent.

* Infrared measurements carried out by Dr. S. F. D. Orr.

TABLE V

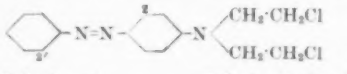
Rates of Reduction with Hydrazine at pH 8



Substituent	Relative Reduction Rate
None	100
3′-COOH	126
4′-COOH	136
3′-CH_3·O	122
4′-CH_3·O	82
3′-Cl	107
4′-Cl	98
3′-Br	97
4′-Br	97
3′-CH_3	109
4′-CH_3	97
3′-Cl, 4′-Cl	103
4′-SO_3H	146

TABLE VI

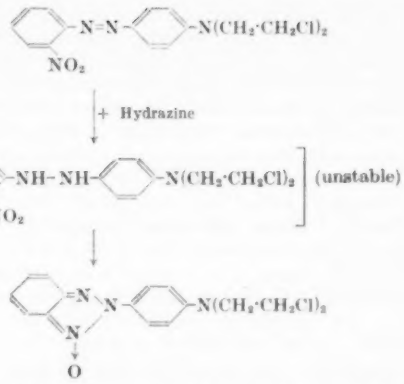
Rates of Reduction with Hydrazine at pH 8



Substituent	Relative Reduction Rate
None	100
2-CH_3·O	468
2-CH_3	359
2-CH_3·O, 2′-COOH	617
2-CH_3, 2′-COOH	519
2′-SO_3H	395
2′-COOH	235
2′-Cl	193
2′-I	189
2′-Br	170
2′-Cl, 3′-Cl	195

There is evidence in this case that, in some instances at least, the first product of reduction was a hydrazo compound, for treatment of the near-colourless solutions with iodine led to a reappearance of azo colour. In support of this finding, it has been known for many years that azobenzene is converted to hydrazobenzene by hydrazine. No attempt was made to isolate hydrazo compounds from the "mustard" derivatives, since 4-dialkylaminohydrazobenzenes appear to be very unstable.

In this case substituents in the *m*′ and *p*′ positions had very little effect on the rate of reduction (Table V). Again, however, there seems to be a slight enhancement in rate when powerfully electron-attracting substituents such as 4′-acetyl and 4′-sulpho are present. But whereas in the case of the stannous chloride reductions *ortho* substituents sometimes decreased and sometimes increased reduction rate, in this case all *ortho* substituents, irrespective of their electronic character or their size, increased the rate of reduction of the azo linkage (Table VI). In the case of the 2′-nitro derivative stannous chloride gave *o*-nitroaniline; hydrazine, however, rapidly reduced this compound to the triazole *N*-oxide, which indicates initial reduction to a hydrazo compound—



The hydrazine reduction rates probably had some similarity to those which could be anticipated *in vivo*, but since *in vivo* reduction is almost certainly enzymic in nature, it was next desirable to ascertain whether any naturally occurring enzyme could effect the reduction of the azo linkage. During the last few months some workers in America [20] have found a liver fraction which seems to contain a fairly specific azo reductase. However, at the time when we were measuring these reduction rates no such system was available, and so we chose to study the xanthine–xanthine oxidase system. Our reason for this choice was twofold— firstly the system is known to reduce various dyes such as Methylene Blue (C.I. Basic Blue 9), and secondly Professor Bergel and his co-workers at the Chester Beatty Institute had available a potent concentrate of xanthine oxidase.

In this case it was necessary to employ purely aqueous solutions, and accordingly only acidic derivatives which have adequate water solubility at pH 8 could be examined.

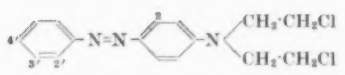
The derivatives, their rates of reduction, and their ability to prevent tumour-growth are shown in Table VII. Here there is a clear-cut correlation between ease of reduction with this enzyme system and ability of the azo compound to inhibit tumour-growth. The reaction did not proceed in accordance with any simple kinetic law, so the results are expressed as the percentage reduction in a given time. Here, again, we obtained evidence that in certain cases a hydrazo compound was the first product formed. We do not necessarily suggest that this enzyme system is the one effecting *in vivo* reduction of azo compounds, but we felt that our results were of interest. Obviously, ease of reduction is not the only factor determining the biological activity of the azo "mustards", and variables such as solubility must be considered.

To summarise, it would seem that in a series of substituted azo "mustards" electron-attracting substituents in the 3′ and 4′ positions increase ease of reduction with stannous chloride, and to a less extent with hydrazine. *ortho* Substituents sometimes increase and sometimes decrease the rate in the case of stannous chloride, and always increase the rate in the case of hydrazine.

The ease with which compounds of the Butter Yellow series are reduced may be of importance in determining the carcinogenicity of a particular dye. It is known, for example, that *NN*-dimethyl-*p*-phenylenediamine is a potent thiol enzyme inhibitor [21], and if this compound were formed in the liver by reduction it might well interrupt important energy-yielding processes in the cell and lead eventually to cancer formation. In fact, this is one of the popular theories to explain azo dye carcinogenesis. As yet, however, no attempt appears to have been made to correlate ease of reduction with carcinogenicity in this series. It is fairly certain anyway that no clear-cut correlation would be forthcoming, because of the complexity of metabolic modification which a molecule might undergo before reduction occurred.

TABLE VII

Rates of Reduction with the Xanthine–Xanthine Oxidase System at pH 8·2



Substituents	Reduction (%) in 30 min.	Activity against Transplanted Walker Rat Carcinoma 256 (A. Haddow)
2-COOH, 4′-NO_2	85*	+
2-CH_3·O, 2′-COOH	70	+
2-COOH, 4′-COOH	55	+
2-CH_3, 2′-COOH	49	+
2-CH_3, 4′-CH_3, 2′-COOH	42	+
2′-COOH	34	+
2-COOH, 2′-CN	34	+
4′-SO_3H	5	−
4-CH_3, 4′-COOH	4	+
4′-COOH	4	−
2′-SO_3H	2	−
3′-COOH	2	−

* In 5 min.

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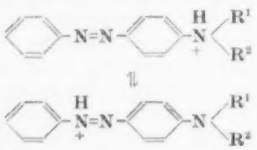
Discussion

Dr. A. BURAWOY: 4-Aminoazobenzene and its derivatives exist in acid solutions as equilibria between the yellow to orange salts (VII) and the red to violet salts (VIII) (originally established by Hantzsch and Burawoy [22] and in more recent years investigated by numerous authors)—

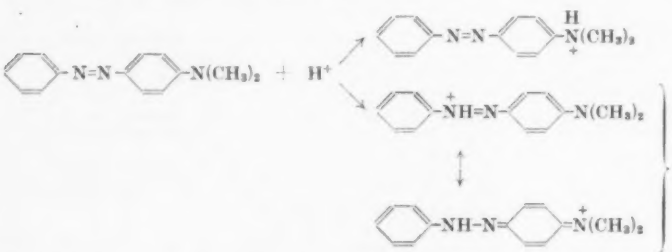


(VII)

(VIII)

Have the authors obtained evidence on the mechanism of the reduction of the bischloroethylaminoazobenzene derivatives in acid solution, in particular, whether the reaction involves the free bases or the salts, and in the latter case, whether there is any relationship between the effect of substituents on the rate of reduction and on the above salt equilibria?

Dr. WARWICK: In studying the effect of acid on the spectra of some derivatives of dimethylaminoazobenzene (Butter Yellow) Badger, Buttery, and Lewis [23] found that the main absorption peaks present in neutral solution and appearing at about 4000 A. were modified in two ways: a new peak normally appeared at about 5300 A., which was attributed to a form (IX) in which the proton had added to the azo linkage, giving rise to a quinonoid structure, and a second peak sometimes appeared at about 3200 A., presumably resulting from proton addition at the amino nitrogen (X)—



(X)

(IX)

In the case of the phenylazo derivatives of bischloroethylaniline we obtained evidence that, when proton addition occurred at all, it did so exclusively at the azo linkage [18]. This was presumably because of the base-weakening effect of the chlorine atoms. At the acidity used in stannous chloride reductions some of the azo compounds (viz. those bearing negative ring substituents) existed almost exclusively in the free azo form, while in other cases a proportion was present in the protonated form. The degree of protonation of the molecule was intimately associated with the nature of ring substituents, electron-releasing substituents increasing the proportion in the protonated form but decreasing the rate of reduction. Since reduction rates of 3′- and 4′-substituted compounds could be fitted on to a Hammett curve, it is tempting to postulate that the deciding factor in determining the reduction rate of a particular compound was the electron density of the azo linkage, and that the degree of protonation was dependent also on this, but not necessarily involved as such in determining reduction rate. Since in no case was any azo compound in a completely protonated or non-protonated form, this part of the question cannot be answered with any certainty.

Dr. L. PETERS: Have the authors examined anionic reducing agents with *ortho*-substituted carboxylic acid groupings? In this case would not the rate of reduction be decreased?

Dr. WARWICK: We did examine sodium hydrosulphite and sodium formaldehyde-sulphoxylate, but found that azo compounds bearing the *o*-carboxyl grouping were still reduced rapidly.

Dr. J. R. HOLKER: Can Dr. Warwick discount the possibility of deactivation of xanthine oxidase through reaction with the nitrogen "mustards" where the apparent rate of reduction was low?

Dr. WARWICK: At this stage this possibility cannot be ruled out entirely, but I think that such enzyme inactivation is fairly unlikely. If inactivation did occur, it is feasible that alkylation by the "mustard" group would be responsible. Owing to the extreme lack of reactivity of the chlorine atoms in the intact azo compound, it is probable that the reduced product, the amine, would be the active species. However, in the case of the 2′-carboxylic acid derivative and the 4′-carboxylic acid derivative, one of which is rapidly reduced and the other slowly reduced, the resulting amine formed by reduction is the same in both cases.

Again, enzyme inactivation by adsorption of the azo compound on the enzyme surface could be postulated. The above examples would illustrate that enzyme inactivation was in some way associated with the presence of a 4′-carboxylic acid group; in this connection it is interesting to note that the azo compound bearing carboxylic acid groups in the 2 and 4′ positions is rapidly reduced, which would tend to discount this possibility. This latter example also rules out the possibility of enzyme inactivation by the other product of reduction, namely *p*-aminobenzoic acid.

Mr. E. STEAD: As the azo compounds with carboxylic acid and sulphonic acid groups gave

rapid rates of reduction, does this not suggest that the solubility in water of these compounds was playing an important part?

Dr. WARWICK: Solubility as such is not a variable which need be considered in determining reduction rate *in vitro*, since completely homogeneous solutions were employed throughout. Solubility is a variable which will affect the distribution of a drug *in vivo*, but of course very little is known about the relationship between water or fat solubility and biological activity in any series of compounds.

The Diazo Reaction in the Coloration of Hydrophobic Man-made Fibres

H. R. HADFIELD and W. F. LIQUORICE

The use of azoic dyes for dyeing synthetic fibres is reviewed, and the application techniques are compared with those employed for dyeing cellulosic fibres. New information is given on the development of azoic combinations on secondary cellulose acetate and Terylene.

The production of a fast dyeing by precipitating into the fibre an insoluble coloured compound is a traditional process in the craft of dyeing. Until 1880, when Thomas and Robert Holliday introduced Vacanceine Red, the production of fast dyeings by the precipitation of insoluble pigments was confined to the use of inorganic materials. A further stride forward in the use of azoic dyes was the introduction in 1912 of arylamides of 2,3-hydroxynaphthoic acid as coupling components to form the basis of the Naphtol AS series [1]. Meanwhile in 1888 Green [2] had discovered Primuline, which, in addition to opening up a new group of thiazole dyes, led to the introduction of a new dyeing technique, which consisted in dyeing the fibre in the usual way, diazotising the dye containing a free amino group, and then developing by treating the diazotised dyeing with a solution of the coupling component.

Stable diazonium salts were prepared by precipitation from solution of complexes of diazonium halides or sulphates with metal halides, the products generally being known commercially as *Fast Salts*.

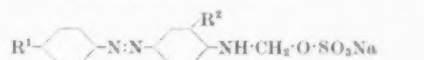
In 1914 stable mixtures of aryl *anti*-diazoates with coupling components were developed (Rapid Fast colours), making use of the discoveries of Schraube and Schmidt [3] and Bamberger [4]. Coupling was effected by treatment with acid. The products were of particular use in printing, and a wide range of colours was produced from different mixtures. The diazoates were later displaced by the more stable diazoamino compounds (triazens). This, again, was a development of earlier knowledge, since Griess himself studied these compounds, and mention of their use was made in 1896 [5]. The ease of development of these mixtures depends on the stabiliser used in the preparation of the triazen, and earlier mixtures of this type required an acid development, but by the use of selected stabilisers products suitable for neutral steam development have been made available.

The above developments in azoic dyes led to their extensive use in dyeing and printing, and it is not surprising that when secondary cellulose acetate was introduced, and later other man-made fibres such as nylon, Terylene, polyvinyl chloride, polyacrylonitrile, and cellulose triacetate, attempts were made to utilise this important class of dyes and the diazo reaction *in situ* for their coloration.

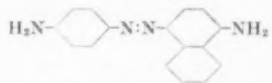
Dyeing Applications

A. SECONDARY CELLULOSE ACETATE

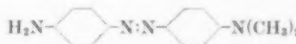
The first new dyes specifically introduced for dyeing secondary cellulose acetate were the Ionamines, discovered by Green and Saunders [6]. They were generally of the formula—



During dyeing, the sulphate group was hydrolysed off. In certain cases the R groups could include a free amino group, which could be diazotised on the fibre and subsequently coupled with a coupling component to yield deep colours of high wet fastness. The Ionamines were soon replaced by disperse azo dyes, which followed the discovery by Holland Ellis [7] that e.g. aminoazobenzene and its derivatives when finely dispersed by grinding with sulphated oils dye cellulose acetate. This soon led to the use of compounds such as—



C.I. Disperse Black 1 (Dispersol Diazo Black B)



C.I. Disperse Black 3 (Dispersol Diazo Black A)

(discovered by Meldola [8] in 1883 and 1884) for the production of blacks on cellulose acetate when diazotised and developed with 2,3-hydroxynaphthoic acid.

2,3-Hydroxynaphthoic acid was discovered by the Chemische Werke von Heyden and used for the production of Ice Blue on cotton cloth in 1891. Its use was suggested by Pokorný [9] in 1893 for the dyeing of protein fibres with azoic dyes, and it was suggested, as a coupling component, for azoic dyes applied to cellulose acetate by Pokorný [10] and Green and Saunders [6] in 1923.

It will be seen that for applying azoic dyes to cellulosic fibres four main methods are available—

Method 1— The Classical Method (discovered by R. Holliday), in which the coupling component is applied first, and the azoic dye developed by treating with a diazotised base.

Method 2— The Inverse Method (first discovered by Green [2]), in which the base is applied and diazotised, and the azoic dye developed by treating with a solution of the coupling component.

Method 3— The Simultaneous Method (the method used by Gurtler [11]), generally known as the *naphthol–nitrite process*, in which the base and the coupling component are applied together, and the azoic dye is developed by treating with nitrous acid.

Method 4— The Modified Simultaneous Method, entailing the application of a diazoate or a triazen along with the alkali-metal salt of the coupling component. On treatment with acid, the diazoate or the triazen gives the diazonium salt, which combines with the coupling component to produce the azo dye.

The first widely used method of applying azoic dyes to cellulose acetate corresponded to Method 2, i.e. the inverse method. This is still used on a very wide scale, but is usually restricted to the production of blacks and very dark navy blues. After application, the base, e.g. Dispersol Diazo Black B, is diazotised by treatment with dilute formic, acetic, hydrochloric, or sulphuric acid and sodium nitrite at 20–25°c. for about 30 min. After rinsing in acidified water, the azoic dye is developed by treating with 2,3-hydroxynaphthoic acid at pH 4·5–5·0. Generally, the sodium salt of 2,3-hydroxynaphthoic acid is used, and the pH then adjusted by the addition of acetic acid. By this means a fine dispersion of the coupling component is achieved. It is an advantage to add a non-ionic dispersing agent to the developing bath before the addition of acetic acid, so that the fine dispersion of precipitated 2,3-hydroxynaphthoic acid is maintained. Development is commenced cold, and then allowed to complete in 30 min. at 60–70°c. As usual with azoic combinations, the material is soaped after development, and with certain combinations, but not with blacks, care is necessary to avoid "blinding" of the azoic pigment [12].

The quantities of acids and sodium nitrite recommended by different workers for diazotisation of the azoic bases applied to cellulose acetate are given in Tables I and II, together with the theoretical relationship for (*a*) conversion to nitrous acid and (*b*) development of the diazonium salt of Dispersol Diazo Black B 300 Powder Fine assuming that the commercial product contains 30% pure dye. It is clear that in practice an excess of acid is added over that required for the complete conversion of sodium nitrite to nitrous acid, and this excess is available for the complete production of the diazonium salt of the base. Generally, the quantities of acid and sodium nitrite recommended are based on the volume of diazotisation liquor, and the excess available is considered reasonable in short liquor ratios, e.g. on a dye jig. If, however, dyeing is carried out on a winch, where a very much longer liquor ratio is used, the quantities of acid and sodium nitrite used are usually in gross excess, and under these conditions it would appear to be desirable to depart from traditional practice and express the quantities of sodium nitrite and acid on the weight of cellulose acetate.

A series of tests was undertaken to determine practically the effect of the ratio of acid to nitrite in the diazotisation of 4% Dispersol Diazo Black B 300 applied to cellulose acetate. After diazotisation under the conditions specified, the colour was

TABLE I

Quantities required for Development of Azoic Dyes on Cellulose Acetate

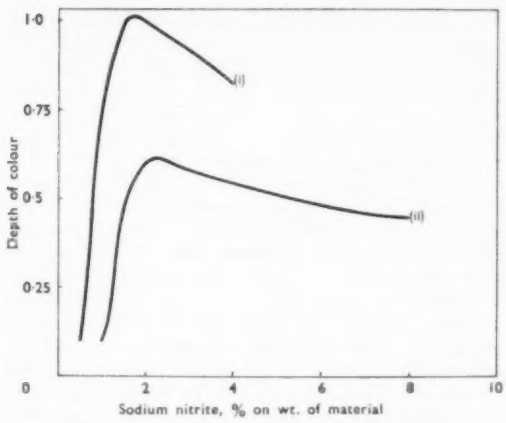
Conditions	Amounts of Reagents				
	$NaNO_2$	HCl (32°Tw.)	Glacial Acetic Acid	$NaNO_2$: HCl	$NaNO_2$: HAc
Theoretical conversion of nitrite to nitrous acid	1	1·7	0·93	1:1·7	1:0·93
Walls [12] (mean conditions)	4/1,000	8/1,000	6·5/1,000	1:2	1:1·6
Mellor and Olpin [13]	4/1,000	—	8/1,000	—	1:2
Green [6]	3/1,000	10/1,000	—	1:3·3	—
ICI [14]	1·5/1,000	4·5/1,000	—	1:3	—
Carmichael and Ivery [15]	3/1,000	6/1,000	—	1:2	—

TABLE II

Quantities required for the Development of Azoic Dyes on Cellulose Acetate

Conditions*	Amounts of Agent required (lb.)					
	$NaNO_2$		HCl (32° Tw.)		Acetic Acid (glacial)	
	40:1†	5:1	40:1	5:1	40:1	5:1
Theoretical to give dibasic salt of base and complete conversion of $NaNO_2$ to HNO_2‡	0·50	0·50	1·6	1·6	0·65	0·65
Walls [12]	16	2	32	4	26	6·4
Mellor and Olpin [13]	16	2	—	—	32	4
Green [6]	12	1·5	40	5	—	—
ICI [14]	6	0·75	18	2·3	—	—
Carmichael and Ivery [15]	12	1·5	24	3·0	—	—

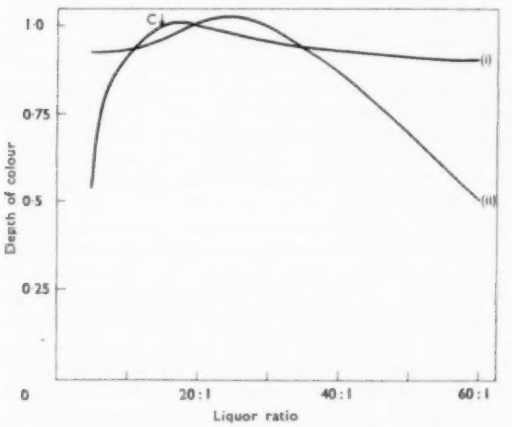
* 100 lb. of fibre and 4% Dispersol Diazo Black B 300 (C.I. Disperse Black 1), giving a dye exhaustion of 70%.
† Winch-dyeing liquor ratio 40:1
Jig-dyeing liquor ratio 5:1.
‡ In these calculations it has been assumed that both amino groups in Dispersol Diazo Black B are diazotised.



(i) 1 mol. $NaNO_2$ + 2 mol. HCl (1:3 weight ratio)
(ii) 1 mol. $NaNO_2$ + 1 mol. HCl (1:1·5 weight ratio)

FIG. 1— Diazotisation of Dispersol Diazo Black B 300 on Cellulose Acetate (Method 2, liquor ratio 15:1)

developed in all cases with an excess of 2,3-hydroxynaphthoic acid at pH 4·5. The depth of the black produced was determined by dissolving the dyed cellulose acetate in acetone and obtaining the optical density at the wavelength of maximum absorption for the solution containing a fixed quantity of the dyed fibre. Fig. 1 illustrates the effect of an increasing quantity of sodium nitrite with two ratios of hydrochloric acid to sodium nitrite. With each ratio of hydrochloric acid to sodium nitrite a maximum yield of black is obtained with 1·5–2·0% of sodium nitrite (corresponding to 1·0–1·3 g./litre in the 15:1 liquor ratio used). This result indicates that in very short liquor ratios as sometimes found in jigger dyeing, certain of the recommendations previously given are deficient in sodium nitrite, even though the quantity is in excess of theoretical. The results also show that a weight ratio of sodium nitrite to hydrochloric acid of 1:3 gives far greater yields than a ratio of 1:1·5, and on this basis it is probable that certain recommendations previously made and given in Table I are not the best, particularly for jig dyeing.



(i) 1·5/1000 $NaNO_2$ + 4·5/1000 HCl (on liquor)
(ii) 2% $NaNO_2$ + 6% HCl (on fibre weight)
C = Control = 2% $NaNO_2$ + 6% HCl at 15:1

FIG. 2— Diazotisation of Dispersol Diazo Black B 300 on Cellulose Acetate (Method 2)

When the quantities of sodium nitrite and hydrochloric acid used to effect diazotisation of Dispersol Diazo Black B are expressed on the volume of liquor, if the quantities recommended are adequate for jigger dyeing, then in using a high liquor ratio, such as is found in winch dyeing, apparently excessive quantities of reagents are used, as is shown by the results in Table II.

A similar series of dyeings to those used to construct Fig. 1 was prepared in which the quantities of sodium nitrite and hydrochloric acid were (*a*) expressed on the weight of cellulose acetate and (*b*) expressed on the volume of the developing liquor. 2% of sodium nitrite and 6% of hydrochloric acid (32°Tw.) were used, and 1·5 g. of sodium nitrite and 4·5 g. of hydrochloric acid (32°Tw.) per litre, which are equivalent when a liquor ratio of 13:1 is employed. An examination of Fig. 2 shows that practically consistent results are obtained when the quantities are expressed on the volume of the liquor, but not when they are expressed on the weight of cellulose acetate if a liquor ratio greater than 15:1 is used. Below this liquor ratio, superior results are obtained if the diazotising agents are used in amounts based on the weight of fibre. It is therefore suggested that in dyeing on the jigger the current recommendations should be replaced by 2% of sodium nitrite and 6% of hydrochloric acid. Under winch dyeing conditions current recommendations, viz. 1·5 g. sodium nitrite and 4·5 g. hydrochloric acid (32°Tw.) per litre, are adequate. This work clearly shows that a large excess of sodium nitrite is required. The reason for this is probably the need to achieve a high concentration of reagents on the surface of the fabric in order to achieve diffusion of sufficient amounts into the fibre in the limited time allowed for diazotisation and also to allow for losses as nitrous fumes.

Method 2 is not the only technique available for applying azoic dyes to cellulose acetate. Rath [16] stated that arylamides of 2,3-hydroxynaphthoic acid were of no value as coupling components for this fibre, but Wallwork [17] and Pokorný [10] give details of techniques which allow arylamides of 2,3-hydroxynaphthoic acid to be used analogous to Method 3 of applying azoic dyes. Wallwork recognised that a higher temperature of 70°C. was essential to allow the arylamides to diffuse into the cellulose acetate, and that they diffuse less readily than the hydroxynaphthoic acid itself.

Attempts have been made, with some success, to use a method analogous to Method 1. Early attempts failed, as, under the conditions used for cellulosic fibres, little coupling component and diazonium salt were absorbed by cellulose acetate. Metzgen and Röhling [18], by applying arylamides of 2,3-hydroxynaphthoic acid to cellulose acetate from a slightly alkaline bath at 70°C. and then treating with a diazonium salt at

30–50°C., obtained development of the azoic pigment in the fibre. This method is not used commercially.

Method 3 has recently assumed even greater importance, as it is widely used for applying azoic dyes to cellulose triacetate, nylon, and Terylene. It appears that the method was first suggested in 1928 [19]. Since that date full accounts have been published by Mellor and Olpin [13], Carmichael and Ivery [15], and Walls [12]. Walls gives much quantitative information, and describes two methods of application.

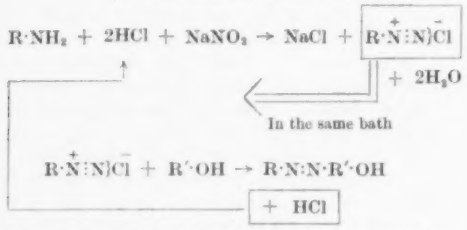
In the development stage the base is diazotised first and then coupling takes place. The quantities of acid and nitrite used are generally the same as those previously given for the Inverse Method, except with certain bases which do not couple readily. Theoretically it should be possible to reduce the quantity of acid employed to half—

(2) INVERSE METHOD

$$R{\cdot}NH_2 + 2HCl + NaNO_2 \rightarrow NaCl + R{\cdot}\overset{+}{N}{:}N)\bar{Cl} + 2H_2O$$

Coupling then effected in a separate bath.

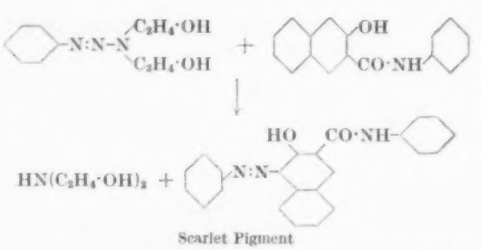
(3) SIMULTANEOUS METHOD



Total requirement of hydrochloric acid one molecule.

Many dye manufacturers market mixtures of bases and arylamides of 2,3-hydroxynaphthoic acid, and these must be applied by the simultaneous method.

Method 4 has been utilised for dyeing cellulose acetate. In the case of cellulosic fibres, as an alternative to *anti*-diazoates the diazo compound is often combined with a secondary amine, e.g. sarcosine (methylaminoacetic acid), and when applied along with an arylamide of 2,3-hydroxynaphthoic acid the development of an azoic pigment is achieved on treating with acid, which liberates the diazonium salt. It is interesting to record that, although the triazens were not developed for commercial use until the early 1930s, Peter Griess made a triazen from diazobenzene and *m*-aminobenzoic acid in 1864 [20]. In 1937 a method was described for using the triazen principle for applying azoic dyes to cellulose acetate: the stabilising amine containing a solubilising group was replaced by one free from sulpho or carboxyl groups, and diethanolamine was favoured. The dyeing technique was to apply from a faintly alkaline dyebath at 70–80°C. an arylamide of 2,3-hydroxynaphthoic acid and a triazen, e.g. that obtained from aniline and diethanolamine, and to develop by treatment with a hot acid solution—



Scarlet Pigment

Satisfactory bulk dyeings were carried out by this technique before 1939. It possesses advantages of simplicity and allows for the production of brighter colours, as there are no coloured intermediates, decomposition products, or nitrosoarylamides left within the fibre at the completion of dyeing. The use of triazens of this type was not developed commercially, however, as the advantages gained did not compensate for the additional cost of the dyes.

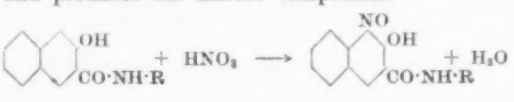
B. NYLON

Azoic dyes have the desirable property of showing good coverage of irregularly dyeing nylon together with high wet fastness properties.

Three methods are used for applying azoic combinations to nylon. Method 2 was first used for the production of blacks using Dispersol Diazo Black B and Dispersol Diazo Black 2BN (C.I. Disperse Black 2) with 2,3-hydroxynaphthoic acid as the coupling component. Diazotisation of the bases is much more difficult on nylon than on cellulose acetate. It is not possible to raise the temperature of diazotisation, as decomposition of the diazonium salt adversely affects the ultimate dyeing. The method used is to double the quantities of hydrochloric acid and sodium nitrite normally used for dyeing cellulose acetate [22].

The use of Method 3 is more convenient, and greater reproducibility is achieved. The base and the coupling component are applied from a highly alkaline bath containing common salt, and development is started cold and finally concluded by treatment at 60°C. for 20–30 min. As is the case for cellulose acetate, better results are obtained with *o*-dianisidine if diazotisation is carried out separately, and development subsequently achieved by treating in a hot buffered slightly alkaline bath [23]. During the past few years the simultaneous method has gradually been replacing the inverse method, particularly for blacks.

Triazens can be applied to the dyeing of nylon by Method 4 [24], hot hydrochloric acid being essential to liberate the diazonium salt. The use of triazens free from solubilising groups is advantageous in its simplicity and for the production of bright reds and scarlets, the additional brightness being due to elimination of one of the main defects observed when azoic combinations are applied to hydrophobic synthetic fibres. During development, in addition to diazotisation of the base the nitrous acid reacts with the coupling component and produces the nitroso compounds—



The nitroso compounds are frequently highly coloured, and as the diffusion rates are low in hydrophobic synthetic fibres compared with cellulosic fibres, they cannot be completely removed by soaping. The presence of e.g. nitroso compounds of arylamides of 2,3-hydroxynaphthoic acid in the completed dyeing is responsible for some dulling of the final colour and, in certain cases, a drop in fastness properties. Ofnaperl Salt RRA (FH) behaves as though it is a triazen of the type indicated, but the constitution has not been published.

C. CELLULOSE TRIACETATE

Azoic dyes are mainly confined, on this fibre, to the production of blacks, although they are also used to some extent for the production of yellows, oranges, scarlets, reds, and maroons. Only two methods are used. Method 2 can be used to produce intense blacks employing Dispersol Diazo Black A (C.I. Disperse Black 3) and 2,3-hydroxynaphthoic acid, but it is not widely used, as it does not readily yield reproducible results and also because Dispersol Diazo Black A does not produce blacks possessing good fastness to heat treatments [25].

Method 3 is the most important method used for applying azoic dyes to cellulose triacetate. At first 2,3-hydroxynaphthoic acid was used as the coupling component, as it was found that, in general, its arylamides were not readily absorbed into the fibre. The use of the acid has drawbacks, as this coupling component is not compatible with many bases used in dyeing. For example, Dispersol Diazo Black B and 2,3-hydroxynaphthoic acid produce a tar, as a result of salt formation, when both are present in the dyebath. To avoid this, it has proved necessary first to apply the azoic base and then, in a separate bath, apply the coupling component [25]. This lengthy technique is clearly undesirable, and to overcome the difficulty a method was proposed using Brenthol OT (C.I. Azoic Coupling Component 18) as the coupling component. Brenthol OT is not readily absorbed into cellulose triacetate, and in many cases the use of a carrier is required in order to achieve adequate exhaustion of the coupling component into the fibre. A detailed method has been published describing the use of diethyl phthalate as the carrier for this purpose [26]. Later work has shown that Brenthol FR (C.I. Azoic Coupling Component 20) is exceptional in behaviour in that, provided a dyeing temperature of 95°c. can be maintained, adequate exhaustion of the coupling component is achieved to enable blacks to be produced without the use of a carrier [27].

Olpin and Wood [28] emphasise the importance of selection of azoic bases which are stable during diazotisation and coupling, as decomposition products can cause heavy staining on adjacent materials, e.g. when the material is subsequently pleated.

The quantities of acid and sodium nitrite recommended for development of azoic combinations on cellulose triacetate are given in Table III. A comparison of the results with those already given in Table I shows that similar concentrations of agents are thought to be necessary. In some recent work the preferred concentrations found were 1 part of sodium nitrite and 1·5 parts of 32°Tw. hydrochloric acid per 1,000 (equivalent to 4% and 6% respectively) at a liquor ratio of 40 : 1. In shorter liquor ratios the amounts would require adjusting by the method suggested for secondary cellulose acetate, and the amounts should be expressed on the weight of fibre.

TABLE III

Amounts of Hydrochloric Acid and Sodium Nitrite required for Development of Azoic Dyes on Cellulose Triacetate

Conditions	$NaNO_2$	HCl (32°Tw.)
ICI recommendation [25]	5–7·5%*	12–20%*
Olpin and Wood [28]	3/1,000	6/1,000

* On weight of fibre.

D. TERYLENE

In general, the use of azoic dyes for Terylene is restricted to the production of full reds, maroons, navy blues, and blacks, but a brown is also possible. Only Method 3 is used. As 2,3-hydroxynaphthoic acid is not compatible with the bases employed for producing blacks, a time-consuming technique was employed, the base being applied first and then the coupling component from a separate dyebath [29]. Work on the high-temperature dyeing of Terylene [30] showed that at 120–130°c. arylamides of 2,3-hydroxynaphthoic acid were absorbed into Terylene. A method utilising the results of the above has been published, and since that time millions of pounds of fibre have been dyed by the new process.

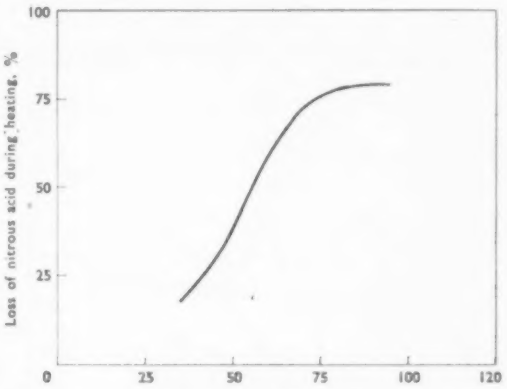


FIG. 3— Loss of Nitrous Acid from a "Diazotisation" Bath heated to Various Temperatures in an Open Vessel (8% sodium nitrite + 6% sulphuric acid for 40 min.)

Fern and Hadfield [30] have made an initial examination of the diazotisation and development conditions for azoic dyes applied to Terylene. In general, development is commenced on a cold bath, the temperature raised to 85–95°c., and the process continued at this temperature for 30–60 min. During this period, between 30° and 60°c. there is a heavy evolution of nitrous fumes from the development bath containing sodium nitrite and mineral acid. The relation between temperature and loss of nitrous acid can be seen in Fig. 3. This evolution

was naturally undesirable, and prompted work on the development process in an attempt to reduce the nuisance to a minimum. One approach investigated was to attempt to diazotise in a cold bath, when the evolution of nitrous fumes is not heavy, and develop subsequently in a hot bath containing sodium acetate. The conclusion was reached that the proposed method was impracticable, and development in hot nitrous acid was essential [30]. However, it is possible in pressurised dyeing machinery, by sealing the machine during development, to prevent the escape of nitrous fumes into the atmosphere. The pressure developed in the machine increases the solubility of nitric oxide and nitrogen dioxide in the liquor at a given temperature, and with certain azoic combinations this produces a greater yield of azoic pigment. For example, using the combination Brentamine Blue B Base (C.I. Azoic Diazo Component 48)→Brenthol FO (C.I. Azoic Coupling Component 19) development at 85°C. in a sealed vessel gives 32% more azoic pigment compared with developing in an open vessel.

The early work was restricted to the use of blue-producing azoic components, as the yield of azoic pigment in the fibre was then most easily measured, for both the base and the coupling component are practically colourless, and the amount of azoic pigment could readily be estimated by determining the optical density of the blue azoic-dyed Terylene dissolved in *o*-chlorophenol. Fig. 4 illustrates the absorption curves of (*a*) Dispersol Diazo Black B and (*b*) the azoic pigment formed when the base is coupled with Brenthol OT (C.I. Azoic Coupling Component 18), undelustred Terylene being used in both cases. It will be seen that, providing the optical density is measured at 590 mμ., the colour of the base will not affect the measurement of the absorption of the azoic pigment produced within the fibre. Using this information, the effect of developing the azoic black over a range of temperatures and in open and sealed vessels was investigated, the results being given in Fig. 5. As in the case of the blue, the advantage of using a sealed vessel is immediately obvious, and, as might be expected, the advantage is greater as the temperature of development is increased.

As there is no possibility of loss of nitric oxide or nitrogen dioxide from a sealed development vessel, it is probable that smaller quantities of sodium nitrite will be required to produce

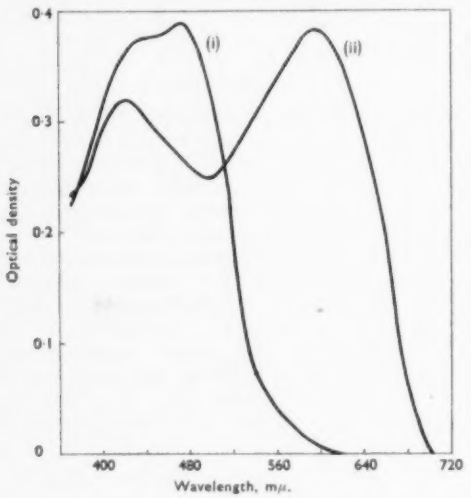


FIG. 4—Absorption Spectra of (i) Dispersol Diazo Black B, (ii) Dispersol Diazo Black B→Brenthol OT Developed Dyeing

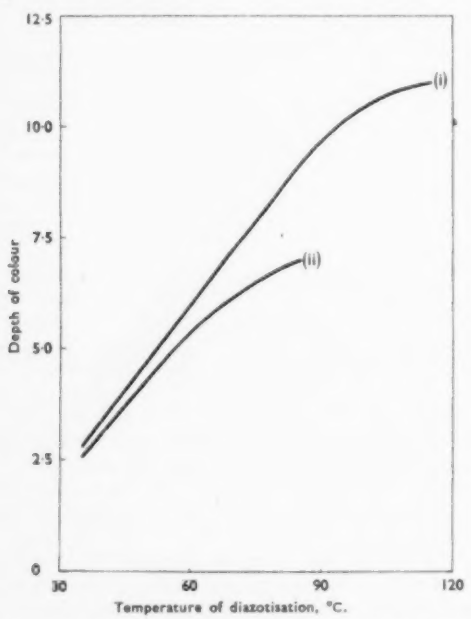


FIG. 5—Comparison of Diazotisation in (i) Closed and (ii) Open Vessels (Dispersol Diazo Black B→Brenthol OT diazotised with 8% $NaNO_2$ + 12% HCl for 40 min.)

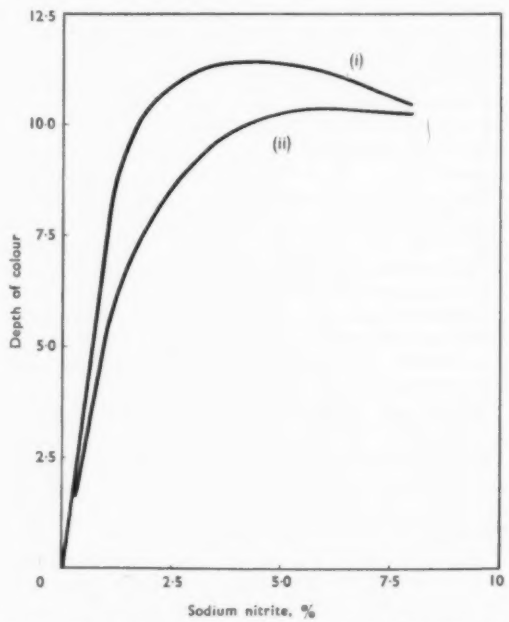


FIG. 6—Effect of Concentration of Nitrous Acid on Development in (i) Closed Vessels and (ii) Open Vessels (Dispersol Diazo Black B→Brenthol OT diazotised with 12% HCl and $NaNO_2$ at 95°C. for 40 min.)

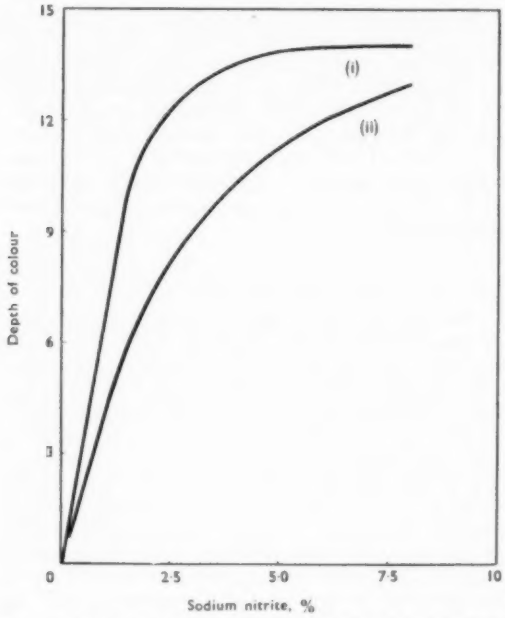


FIG. 7—Effect of Concentration of Nitrous Acid on Development in (i) Closed Vessels and (ii) Open Vessels (Brentamine Blue B Base→ Brenthol FO diazotised with 12% HCl and $NaNO_2$ at 95°C. for 40 min.)

maximum development of colour. It will be seen from Fig. 6 and 7 that, not only are higher yields possible if development is carried out in sealed vessels, but very large reductions in the quantity of sodium nitrite required are also possible. For example, in the two cases examined, 2–3% of sodium nitrite used in sealed vessels gives the same result as 6% of sodium nitrite in open vessels. The use of reduced quantities of sodium nitrite in sealed vessels has been confirmed in bulk dyeings. It has also been found that, in the case of the black, if the quantities of sodium nitrite used are not reduced, off-tone blacks are produced. This effect may be due to some oxidation of the azoic pigment by the high concentrations of nitrogen oxides in the fibre, resulting from the high concentration of nitrous acid in the bath made possible by the pressure developed in the sealed vessel.

The use of hydrochloric acid, in conjunction with sodium nitrite, for developing azoic dyes has been common for many years. It is generally considered, however, that the stainless steels used in dyeing machine manufacture are less resistant to hydrochloric acid than to sulphuric acid. Grundy [31] does not supply any information on hot developing liquors, and the information published by stainless-steel manufacturers does not show any difference, under the conditions of test, between hydrochloric and sulphuric acids. Some tests to compare the resistance of stainless steels have been carried out in an open vessel at 85°C. for 12 hr. with sodium nitrite initially present in the liquor. The concentrations correspond to those used in developing azoic dyes on Terylene. It will be seen (Table IV) that sulphuric acid does not affect the

TABLE IV

	Type of Stainless Steel	Loss in Weight (g./sq.ft.) $NaNO_2$ + HCl	Loss in Weight (g./sq.ft.) $NaNO_2$ + H_2SO_4
(1)	Titanium-stabilised steel 18/8 to *B.S.* 970, EN 58B	1·66	0·01
(2)	Niobium-stabilised steel 18/8 to *B.S.* 970, EN 58G	1·21	0·01
(3)	Molybdenum-bearing 18/10 stainless steel to *B.S.* 970, EN 58J	0·08	0·01
(4)	Unstabilised 18/8 low-carbon (0·052% C) steel to *B.S.* 970, EN 58A	5·6	0·03

stainless steel to the same extent as hydrochloric acid, and that certain steels are seriously attacked by hydrochloric acid. However, a steel such as (3), which is usually employed in dyeing machine construction, is not seriously attacked even under the excessively severe conditions of the test.

A comparison has been made between hydrochloric acid and sulphuric acid in promoting the development of azoic dyes on Terylene. Fig. 8 shows the effect of varying amounts of sulphuric acid and hydrochloric acid on the development of an azoic black. On a weight basis, sulphuric acid (68°Tw.) is twice as strong as hydrochloric acid (32°Tw.) over the range of concentrations examined (2–20% hydrochloric acid and 1–10% sulphuric acid, both on weight of fibre). The

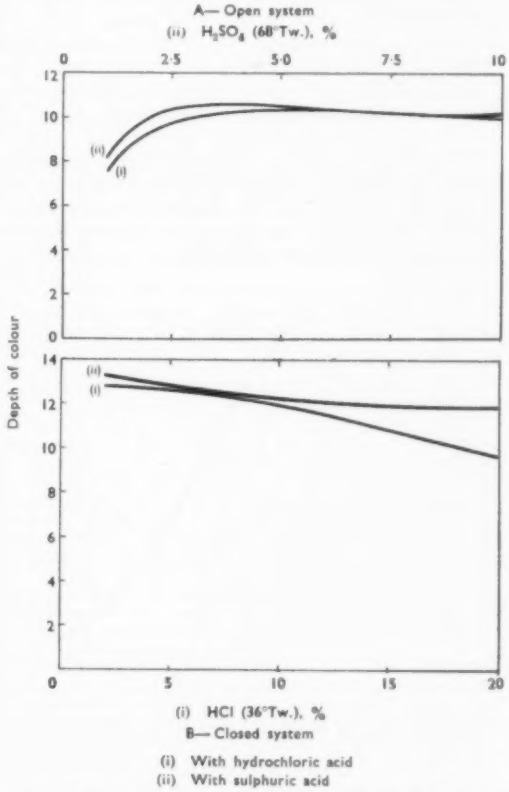


FIG. 8—Effect of Acid on Development on Terylene (4% Diapersol Diazo Black B 300 powder fine→ 2·5% Brenthol OT diazotised and coupled at 85°C. for 40 min.; 8% $NaNO_2$ in 30:1 liquor)

system is evidently insensitive to the quantity of acid used, in both sealed and open vessels, and, practically, hydrochloric acid and sulphuric acid are interchangeable.

In developing azoic dyes on Terylene, the quantities of acid and sodium nitrite used are normally expressed on the weight of fibre. Work has been carried out to determine whether this is preferable to expressing the quantities on the volume of liquor. The results showed once again that the system is very insensitive: only in short liquor ratios ($< 15 : 1$) is there a marked preference for calculating the quantities on the weight of fibre, and in very long liquor ratios ($> 60 : 1$), such as might be found in the dyeing of a Terylene–cellulosic fibre blend, there is a preference for calculating the quantities on the volume of liquor. Under these conditions 1 part of sodium nitrite and 2 parts of hydrochloric acid (32°Tw.) per 1000 are suggested.

TABLE V

Tendering in 50:50 Terylene–Cellulosic Fibre Blends

Conditions*	Fluidity of Cellulosic Component	
	Cotton	Viscose Rayon
Control	4·3	8·9
Blank dyeing with 20% NaCl	4·0	10·2
Before development of dyeing	6·6	9·7
Complete dyeing (dyeing, development, soaping)	12·1	14·3

* Time of development = 40 min.
Temperature of development = 85°c.
1/1,000 $NaNO_2$
2/1,000 HCl (32°Tw.)
Scoured and soaped before drying.

When Terylene–cotton or Terylene–viscose rayon blends are dyed black with Dispersol Diazo Black B and Brenthol FR (C.I. Azoic Coupling Component 20), some tendering of the cellulosic component results (see Table V).

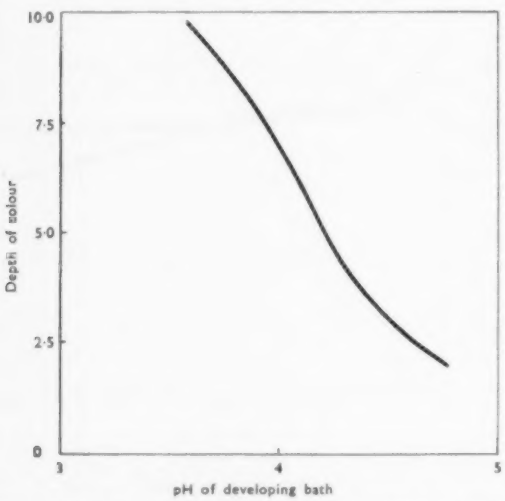


FIG. 9—Effect of pH on Development on Terylene (4·0% Dispersol Diazo Black B 300 powder fine–2·5% Brentosyn OT, diazotised and coupled using 6% $NaNO_2$ in a 30:1 liquor, buffered where necessary with sodium acetate, at 85°c. for 40 min.)

It is considered that the extent of degradation is not serious in the case of viscose rayon and can be tolerated, but it would obviously be preferable to avoid degradation if possible. One approach would be to reduce the acidity of the dyebath, but Fig. 9 shows that any increase in pH above that obtained with hydrochloric acid and sodium nitrite alone results in a serious loss in tinctorial yield. This approach is therefore considered impracticable.

E. TEXTILE PRINTING

The application of azoic combinations to non-cellulosic hydrophobic fibres by printing has not met with any degree of success because of the slow rate of penetration of the components into the fibre. Printing a mixture of the coupling component in a caustic alkaline solution with a stabilised diazo compound, e.g. a diazoamino compound, has been proposed for the printing of cellulose acetate and polyamide fibres[32] using a specific stabiliser for the diazo compound. The prints are fixed by steaming, and coupling is effected by a subsequent acid treatment. A modification of this method consists in the use of a basic organic solvent, such as β-diethylaminoethanol, as the coupling component together with commercially available stabilised diazoamino compounds and azoic coupling component mixtures. Good fixation is obtained on cellulose acetate and nylon by neutral steaming only, although the resulting light fastness is lower than on cellulosic fabrics.

A further alternative, which has been used for Terylene, particularly for the production of a fast azoic black by mélange printing, is printing with a mixture of a free amine and a coupling component in the free hydroxy form followed by steaming and subsequent diazotisation at an elevated temperature. To ensure adequate penetration it is necessary to steam under pressure. The base normally employed for the production of blacks on Terylene (C.I. Disperse Black 1) is relatively volatile in steam, and thus gives rise to marking off and diffuse edges to the prints. The process is therefore not generally applicable to the printing of fabrics. However, in mélange printing, where definition is less critical, a good black is obtained by the application of a mixture of Dispersol Diazo Black B and Brenthol OT. A mixture of the base and the coupling component in the free hydroxy form is prepared as a slightly thickened aqueous dispersion, and after printing, the slubbing is steamed for at least 1 hr. at 1·4 kg./sq.cm. (20 lb./sq.in.). Diazotisation is then brought about by treatment in sodium nitrite and hydrochloric acid, the temperature being raised to 90–95°c. and held at this value for approx. 30 min. The rate of development is increased by carrying out the process at a higher temperature. The final stage of the process is the removal of any unpenetrated pigment by a caustic soda–hydrosulphite reduction bath to ensure maximum fastness to rubbing and washing[33]. It is of interest that coupling takes place with the free hydroxy form of the coupling

component, not the ionised form as is usual in azoic reactions.

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Concluding Remarks

CLIFFORD PAINE

And so, after an intensive day, we come to the close of a notable Symposium among the many which the Society of Dyers and Colourists has arranged over the years. During the day we have passed from a picture of the life and times of an individual to a modern scientific study of the reactions in which that individual scientist was especially interested, and have finally touched upon some limited aspects of the technological implications of his work. It is no part of my duties to attempt to summarise the papers that have been read today or even to focus your attention on some of the highlights from them. You will perhaps in these closing stages permit me to re-examine briefly why we have held this Symposium today and why, in fact, we are honouring the name and the memory of Peter Griess.

It is certainly not because he was some great flamboyant personality who could not at any stage of chemical history be overlooked. It is not, I venture to suggest, merely or primarily because of his scientific work, solid and sound though that was, requiring as it did the handling of difficult unstable compounds at a time when the knowledge of systematic structure was limited and often faulty. It is noteworthy that the volume of Liebig's *Annalen* which contained Griess's first paper contained also an early paper by Kekulé which made clear the quadrivalent nature of carbon. There are many who have covered a wider range of investigations and with more versatility without leaving as deep a mark as Peter Griess. Our interest in the man and his work stems, I think, from our realisation, looking in retrospect over a hundred years, that the repercussions from Griess's work, particularly in the fields of technology, have been so impressive. It is to this aspect that our Symposium today has done, perhaps, rather less than justice. We have not so far reminded ourselves of the part which azo dyes played in the early anti-bacterial work or that the modern sulphonamides began with Prontosil Rubrum, an azo dye of which Peter Griess can be considered the grandfather. The influence of Griess's work on the development of dye technology can, of course, hardly be overestimated. Perhaps you will permit me to quote something which I said in another place during the Perkin Centenary celebrations—

> The diazotisation and coupling reactions afford a relatively simple means of building colour units with systematic variations in structure which has proved quite invaluable to the dyestuffs chemist. By systematic and sometimes tedious examination of the various permutations and combinations possible by this technique there has been amassed a considerable amount of knowledge of the broad relationships between dyestuffs structure and properties in this series. This has given the dyestuffs research worker principles by which to forecast overall properties. More important, it has enabled him to devise an appropriate compromise of properties for the fulfilment of a particular technological purpose. For example, by proper choice of the number and disposition of sulphonic acid groups and other structural features it is possible to arrive at a compromise balance in affinity for cotton and wool which has value in the dyeing of mixed fabrics. Similarly it is possible to design azo dyestuffs with comparable rates of dyeing so that the dyeing of mixtures can be more effectively controlled. The same tools enabled the problem of dyeing cellulose acetate to be solved and the principles of affinity for this and other new fibres to be elucidated.

Griess himself had little or no flair for technology, and the industrial significance of his work is entirely due to other contemporary pioneers.

Certainly Griess's original technique of diazotisation, left unchanged, would never have been a serious industrial large-scale technique. We take for granted the simple and elegant technique of diazotising a base in an acid aqueous medium using sodium nitrite solutions. Curiously enough, the originator of this simple device, as far as I can determine, remains in confused obscurity. In Meyer and Jacobson's *Chemistry*, 1902 edition, it is referred to as "The simple process first described by Victor Meyer and Ambühl", but no date and no reference is given other than a reference to a paper by Knoevenagel, which in any case only described diazotisation in alcohol with amyl nitrite. Other textbooks around the same period give equally misleading or inaccurate references copied from one to another. In more recent times Saunders attributes the first use of sodium nitrite for diazotisation to Martius, yet the reference given is nearly thirty years after Griess's discovery, and in any event deals with a special method of making diazoamino compounds.

You may feel that I am worrying about biographical trivia, but I believe that there are two important morals in the situation. The first is that in the documentation of our scientific and technological progress we all too often overlook the rôle of the technologist in converting the exotic techniques of the laboratory into a useful industrial operation. The second is a reminder to the young chemist just starting his career in industry that in industry pure science, however good, is not enough unless illuminated by that practical imagination capable of scaling up a laboratory reaction with simplification and elegance.

But to return to Peter Griess, the prime cause of our Symposium today. My own mind goes back to the 1920s, when as a young chemist I thought that I had discovered the apparent migration of a diazo group in coupling diazotised sulphanilic acid with toluidines and xylidines. I found that the end-products were sulphanilic acid itself and the diazotised toluidine or xylidine. I remember my disappointment when I found that I had merely rediscovered something which Griess himself had recorded in the *Berichte* in 1882. Most chemists at some time or another have had similar experiences, but they are experiences that give one a new respect for the earlier author. My own experience gave me a renewed and personal interest in the detailed researches of Peter Griess, which enhances my pleasure and sense of privilege in the opportunity of making the closing remarks at a Symposium in his honour.

The implications of Peter Griess's work are by no means exhausted. Technologists will find as many new applications of it in the future as they have in the past.

CORRESPONDENCE

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The Isoequilibrium Temperature in Dyeing

It has been shown [1] that changes in structure of a dye alter both the energy ΔH and the entropy ΔS of dyeing, and that large values of ΔH tend to accompany large values of ΔS. This tendency attains the precision of a linear relationship [2–4] between ΔH and ΔS. It is not clear whether this applies to acid dyes on wool, but the purpose of this note is to discuss the significance of the relationship in the light of the results available for the dyeing of cellulose fibres with direct [2] and azoic [4] dyes and of cellulose acetate and nylon with disperse dyes [2, 3].

The above relationship may be defined by the linear equation—

$$\Delta H = \Delta H_0 + \beta \Delta S \qquad \text{(i)}$$

where ΔH_0 is simply the intercept or value of ΔH corresponding to $\Delta S = 0$, but has no physical meaning; the slope β is a quantity having the dimension of temperature. The free energy of dyeing, which determines the equilibrium at any temperature, is given by—

$$\Delta F = \Delta H - T\Delta S \qquad \text{(ii)}$$

Combination of (i) and (ii) gives—

$$\Delta F = \Delta H_0 - (T - \beta)\Delta S \qquad \text{(iii)}$$

When $T = \beta$, $\Delta F = \Delta H_0$, and all the equilibrium constants are the same within the precision of the relationship. Hence β is called the *isoequilibrium temperature*, and equation (i) the *isoequilibrium relationship*. These concepts have been discussed in connection with general organic reactions from a theoretical point of view by Evans and Polanyi [5] and from a practical standpoint by Leffler [6].

Of course, if β differs greatly from the usual working temperature, the relationship may be invalidated by changes in ΔH with temperature. In that case β is merely a slope and has no physical meaning.

From the possible existence of an isoequilibrium temperature it is clear that care is necessary in the interpretation of the effect of dye structure on the dyeing equilibrium. If the temperature chosen is close to the isoequilibrium temperature, it is not safe to conclude from the constancy of the equilibria that the change in structure of the dye has no effect. However, we might consider the possibility of a kind of Hammett's constant for the dye molecule.

The author expresses his thanks to Dr. J. E. Leffler for his paper and Dr. K. Konishi and Dr. N. Kuroki for their directions.

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3rd March 1959

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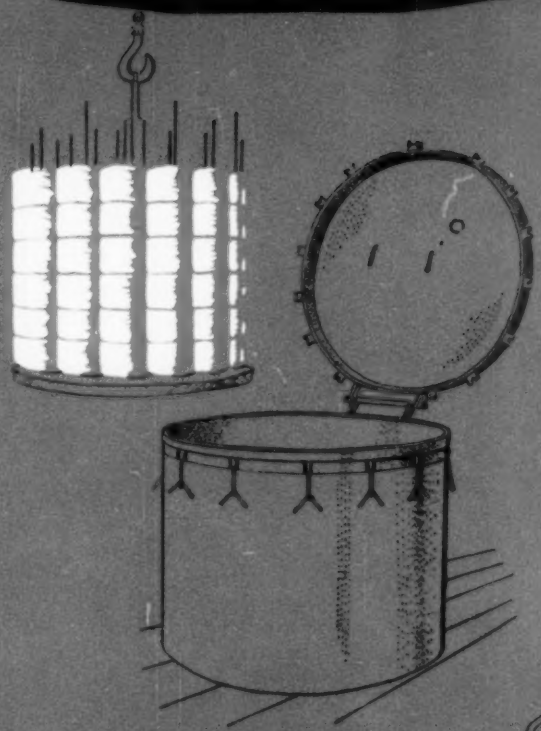

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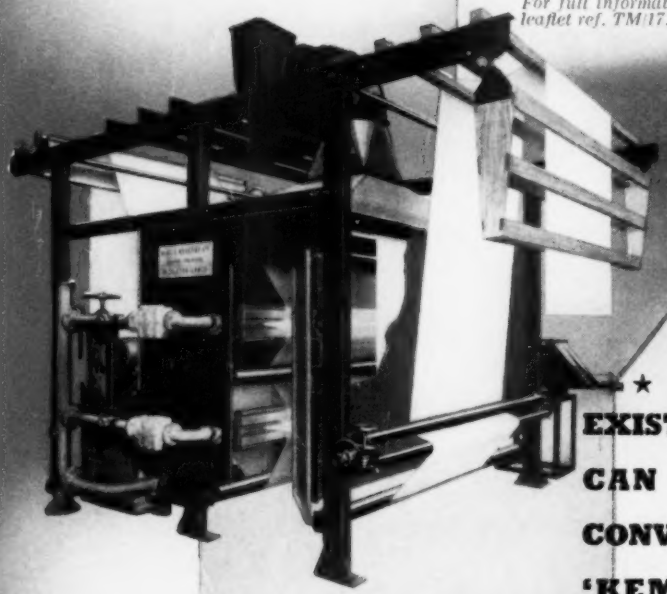

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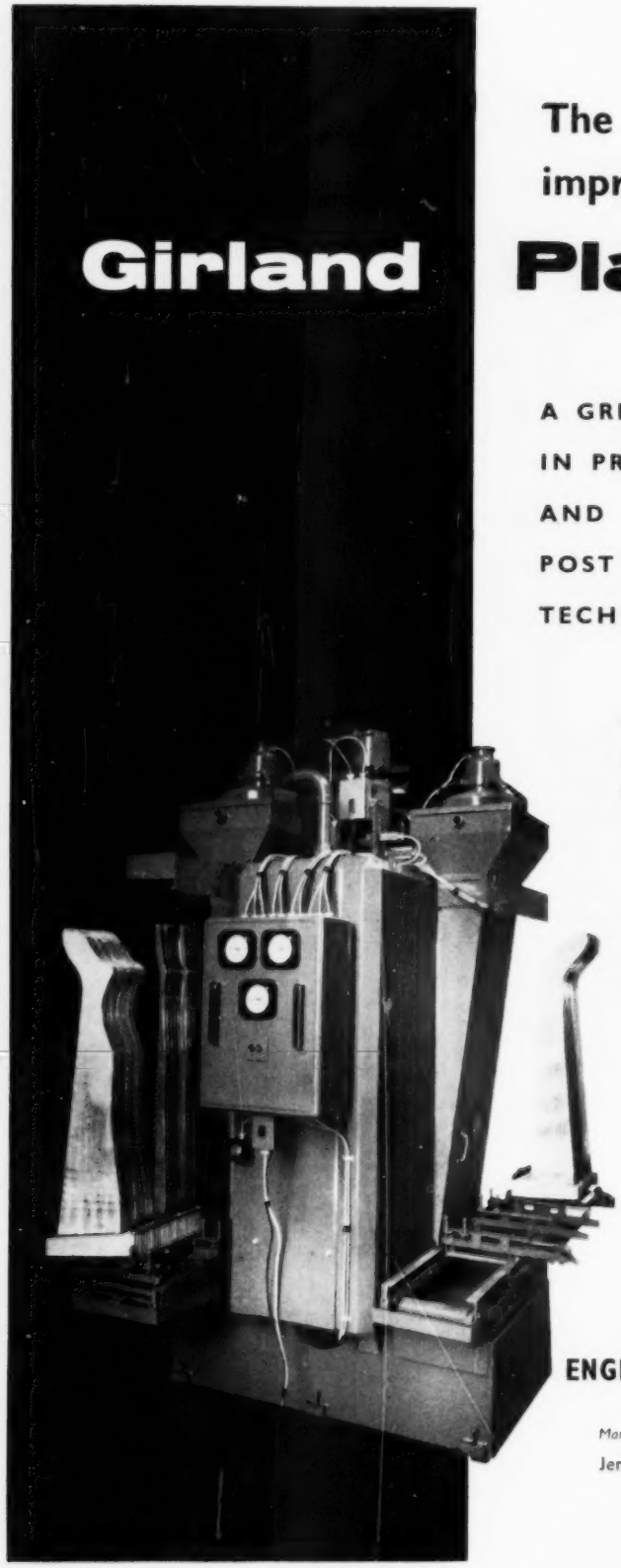

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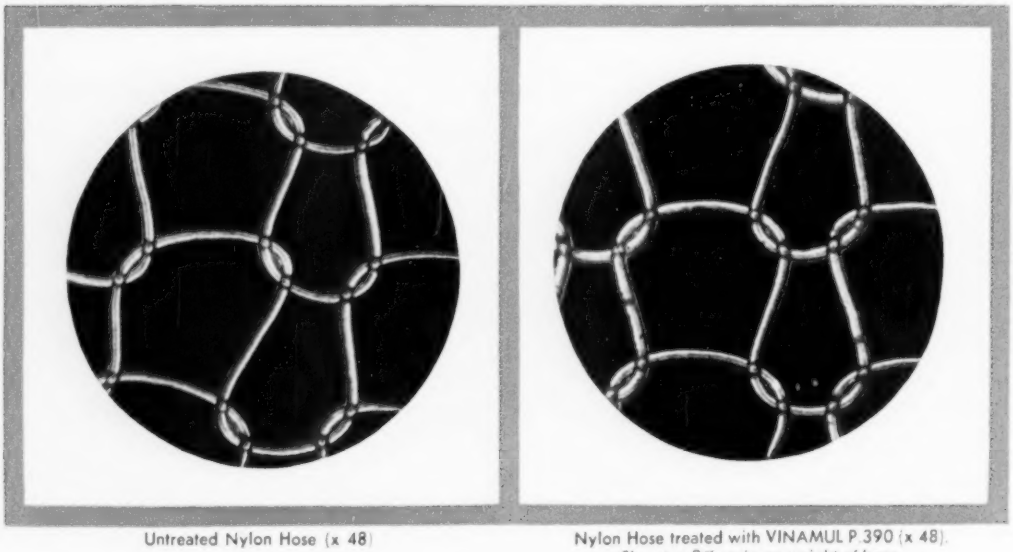

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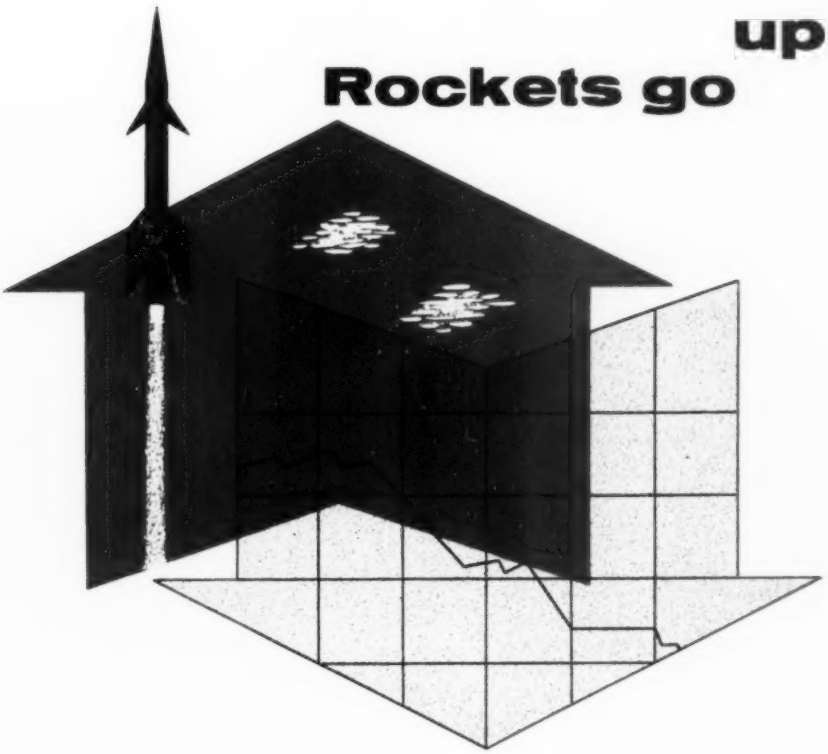

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51

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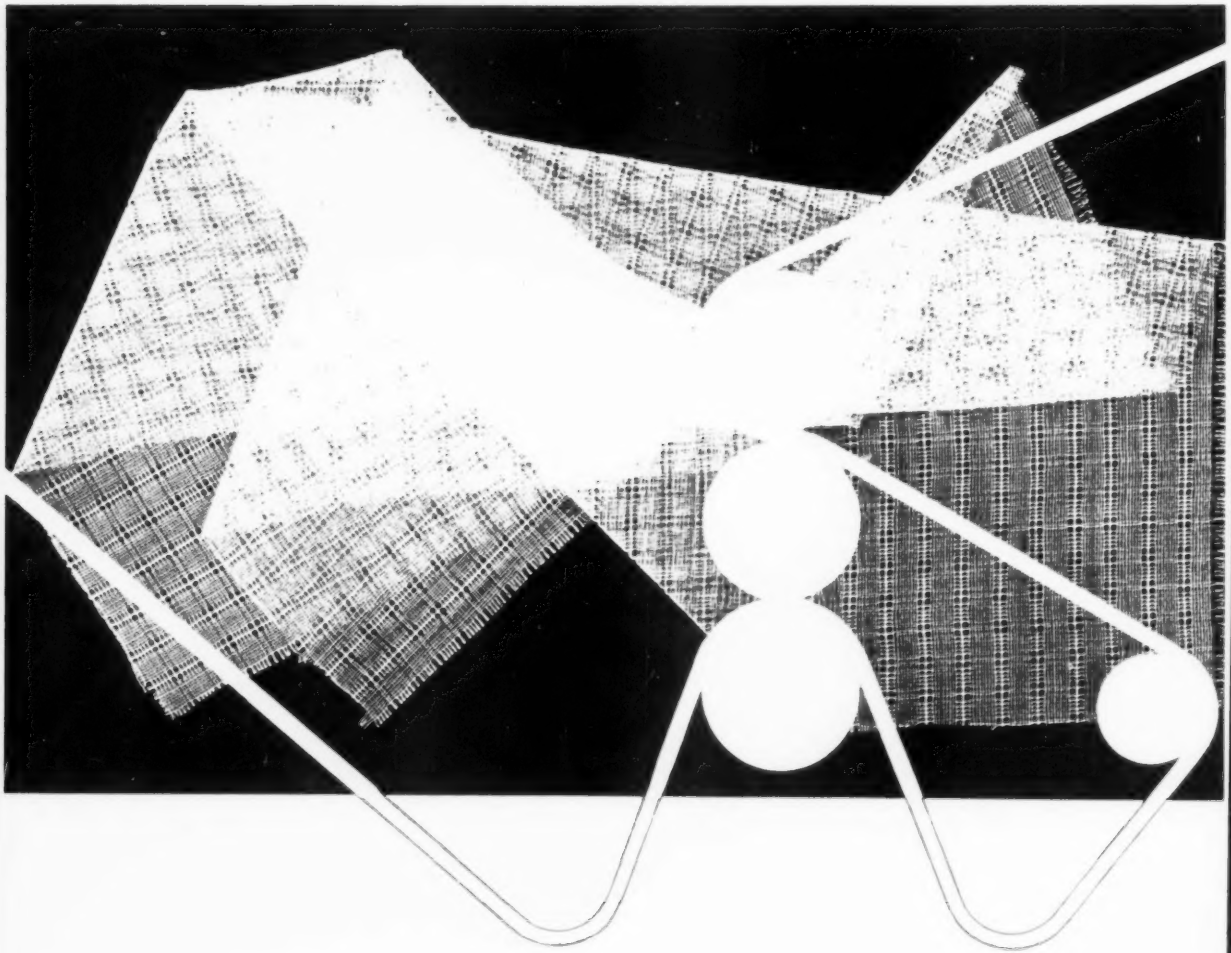

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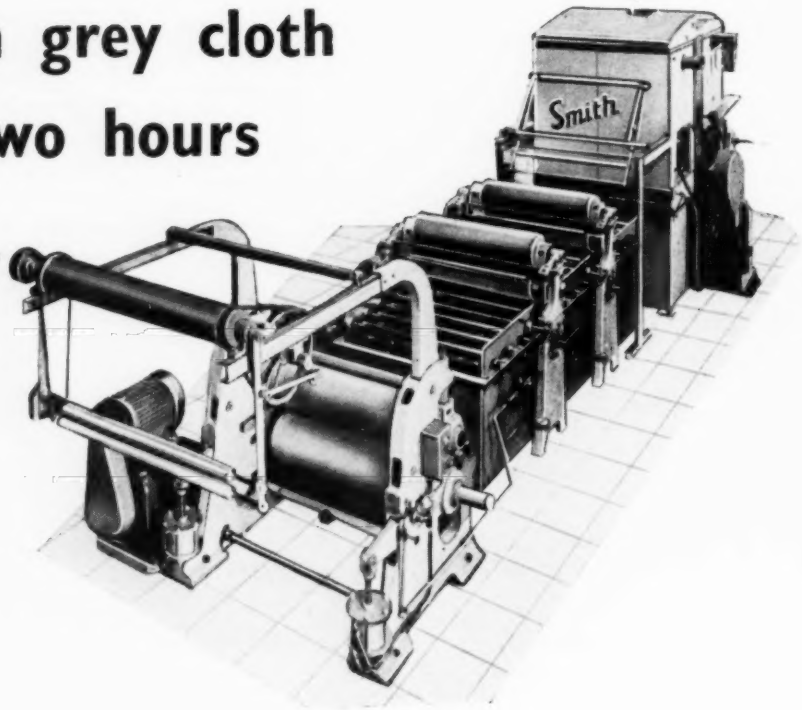

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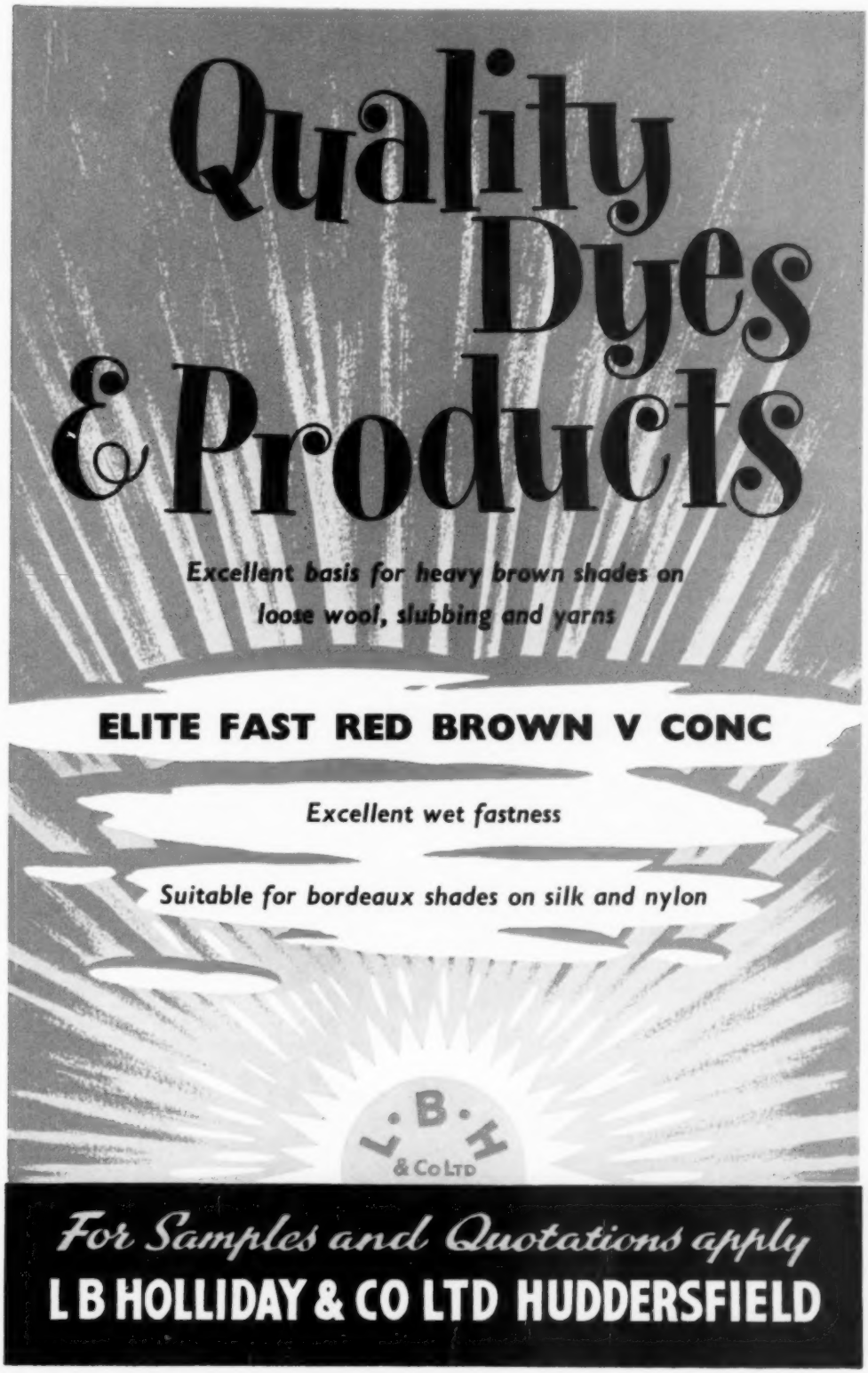
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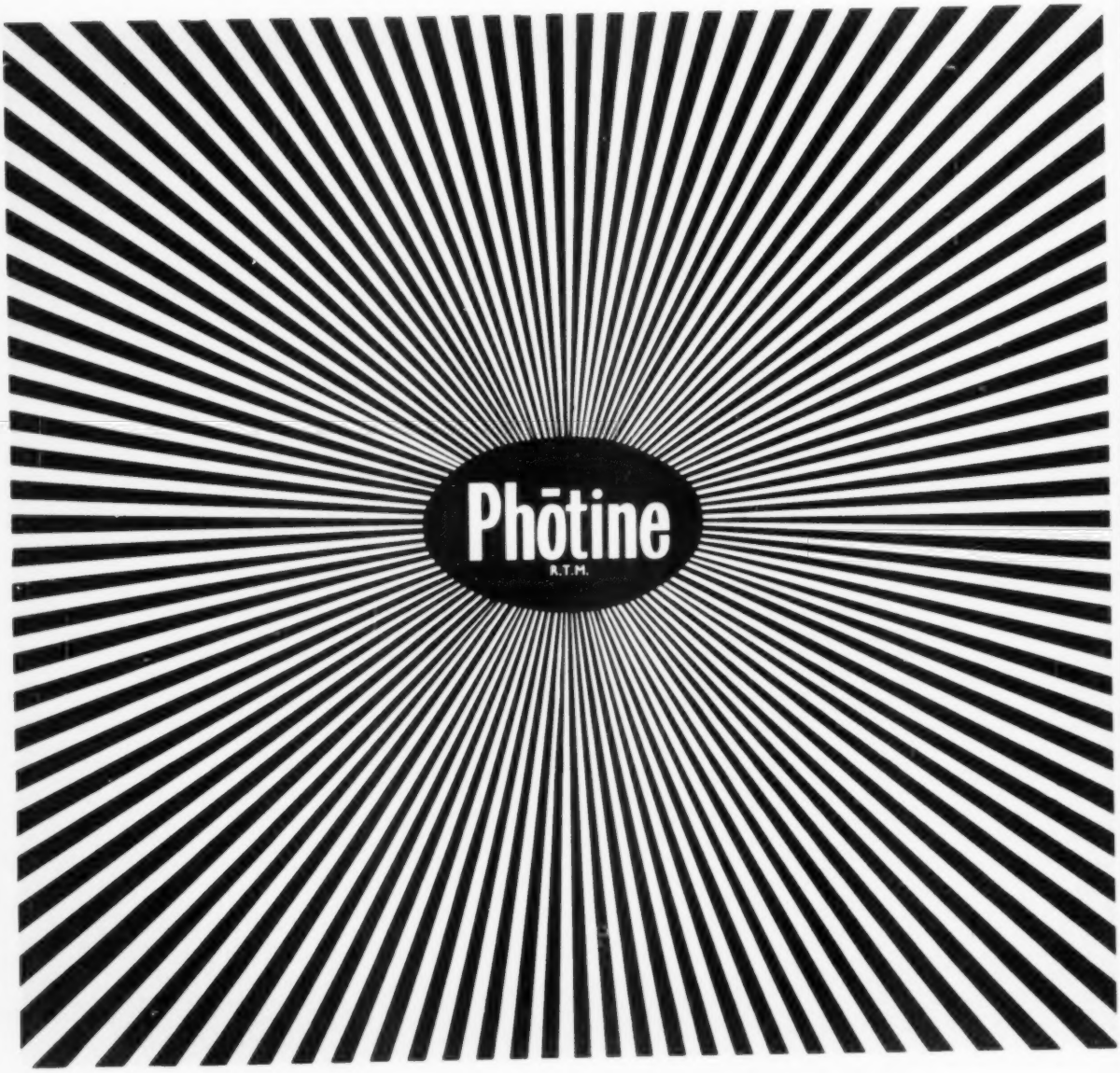

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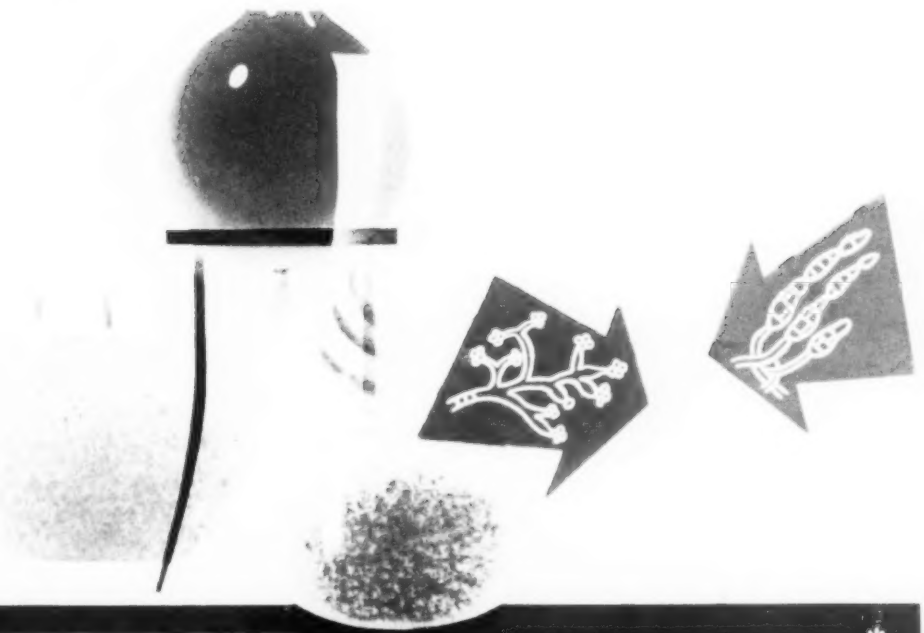

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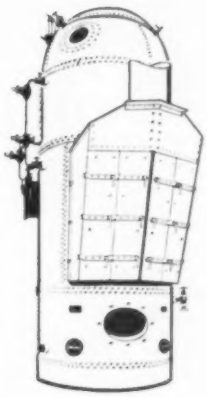

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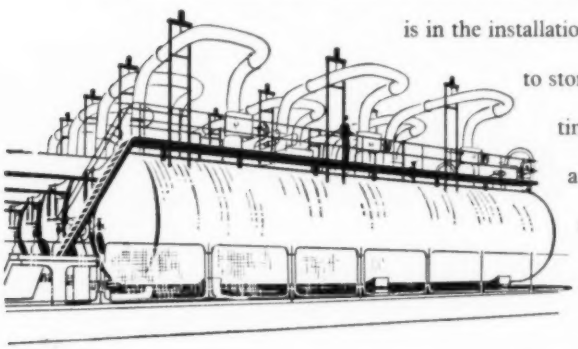

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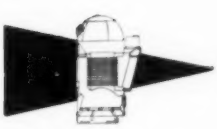

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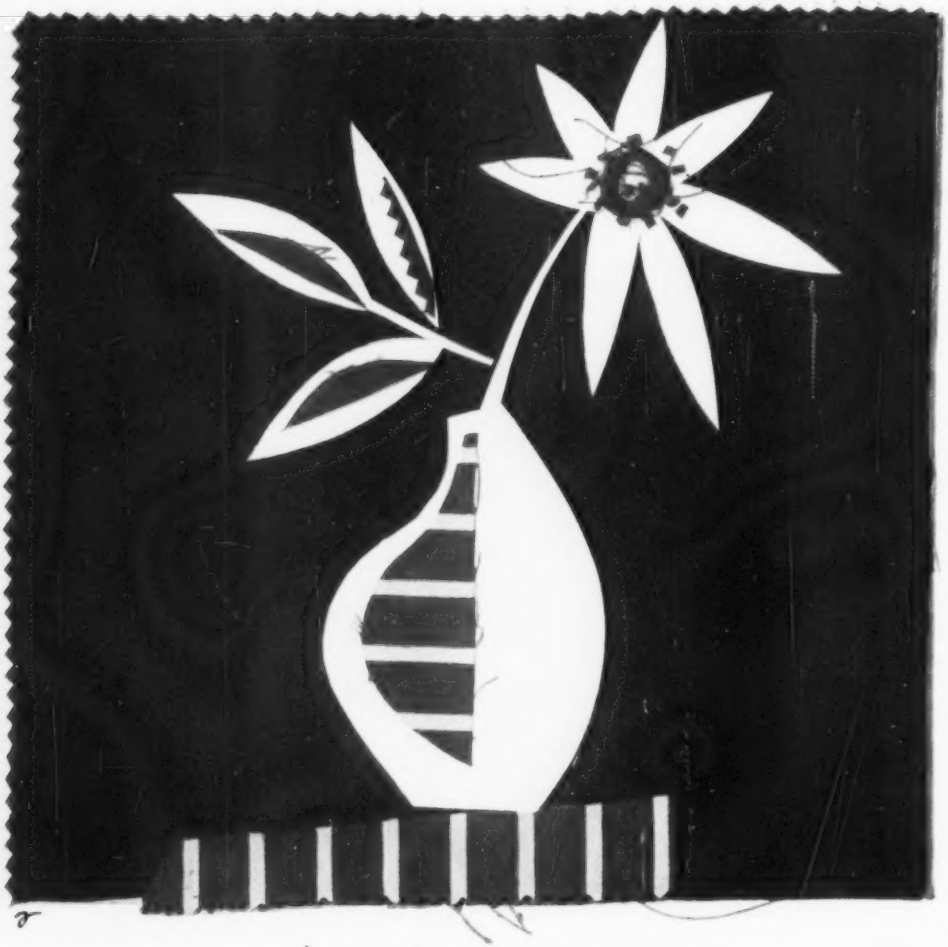

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Hydroxylamine in the High-temperature Dyeing of Acrylic Fibres

The publication during the past year of several patents covering the use of hydroxylamine in the dyeing of acrylic fibres, both in the presence and in the absence of copper ions, shows that a number of research groups have worked out similar processes independently. However, recent investigations cast doubt on the explanation, put forward by Khachoyan and Niederhauser [1] and by other workers, that the improvement in dyeing properties is due to formation of amino groups in the polymer.

The following claims have been made in eight recent patents —

(1) A process for dyeing polyacrylonitrile fibres with acid or direct dyes in the presence of a copper salt and hydroxylamine at 90–120°c.[2].

(2) A process for dyeing polyacrylonitrile (including fibres) by treatment in presence of a reducing agent (e.g. hydroxylamine) and copper complexes of *oo'*-dihydroxymonoazo dyes containing only one sulpho group, a similar process in which dyeing is carried out by the cuprous ion technique, and the use of copper salts, reducing agents, and the corresponding metal-free dyes [3].

(3) Improvements in the dyeing properties of polyacrylonitrile by treatment with aqueous hydroxylamine at pH 7–10 [4].

(4) Production of polymeric material by reaction of hydroxylamine with polymers containing nitrile groups [5].

(5) Improvement in affinity for dyes of polymeric material containing nitrile groups by reaction with hydroxylamine [6].

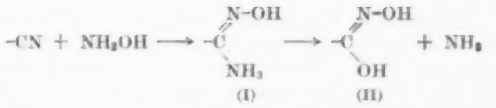
(6) Improvement in affinity for dyes of acrylic fibres by treatment with hydroxylamine [7].

(7) Improvement in dyeability of acrylic fibres by treatment with neutral aqueous hydroxylamine or with neutralised solutions of hydroxylamine salts [8].

(8) Process for dyeing acrylonitrile and vinylidene cyanide polymers, with dyes other than copper complexes of monosulphonated *oo'*-dihydroxymonoazo dyes, in the absence of copper salts and in the presence of hydroxylamine at temperatures above 80°c., preferably above 110°c.[9].

From the above it is clear that the process of improving the dyeability of acrylic fibres by treatment with hydroxylamine in the absence of copper atoms or ions forms the subject of at least five patents or patent applications.

We have prepared a new class of polymers by the action of hydroxylamine on polymers containing nitrile groups [10], and have found that, in dimethylformamide medium, the reaction results effectively in the formation of amidoxime groups [11]. In aqueous medium, on the other hand, the primary reaction is immediately followed by hydrolysis [12] of the amidoxime groups (I) to hydroxamic acid groups (II)—



Starting with polyacrylamidoximes, the hydrolysis in alkaline medium comes to a standstill when about 55% of the amidoxime groups have been hydrolysed [13]. Although this does not necessarily imply that in a polymer containing only a few hydroxamic acid groups (about 5% in the examples given by Khachoyan and Niederhauser [1]) hydrolysis is similarly incomplete, our experience in this field leads us to question whether the method of analysis proposed by Khachoyan and Niederhauser [1] gives an accurate idea of the proportion of groups able to improve the dyeability. In any event, we cannot agree with their proposed reaction scheme for the alkaline treatment.

The extent of reaction can be estimated more simply, and certainly more accurately, either by potentiometric titration of the hydroxylamine remaining in the reaction medium or by hydrolysis of the polymer in strongly acid medium (4N. hydrochloric acid) followed by potentiometric titration of the liberated bases.

The hypothesis of the formation of heterocyclic rings, as suggested by these authors, is justified only when most of the nitrile groups are converted into amidoxime groups; it is certainly not justified if degrees of conversion as low as 5% are to be considered [cf. 14].

The characteristic feature of the process claimed by Francolor [9] seems to be the use of dyeing temperatures above 100°c. In order to show this improvement, Khachoyan and Niederhauser collected different results [15], from which it was concluded that, surprisingly, the exhaustion of the dyeing bath is more complete if the treatment and the dyeing are carried out at about 125°c.

This conclusion does not seem to be fully justified. First it must be remembered that, as the reaction rate increases when the temperature is raised, one can normally expect that in a given time interval a larger amount of polymer will be converted; consequently improved dyeability will be observed when the process is carried out at higher temperatures. Hence the improvement appears to be rather a necessary consequence of the above chemical principle and lacking in any inventive step.

Furthermore, we contest the value of conclusions based on experiments in which more than one variable is changed. This is certainly the case here, as both the nature of the hydroxylamine salt and the liquor ratio as well as the pH are different. The pH value, especially, which is known to have a marked influence upon the exhaustion of a dyebath, could explain the difference in exhaustion in the two sets of experiments.

Contrary to M. Khachoyan's answer [16] to Dr. Lister's question, we have found that the dye uptake is proportional to the amount of hydroxylamine used.

Although at first sight it seems very attractive to explain the improvement in dyeability by the presence of the amino groups in the amidoxime groups [1], it appears that in the treated fibres the nitrile groups are partially converted into hydroxamic acid groups [11]. Hence the fixation of the dye molecules must take place on the hydroxamic acid groups.

Summing up, we may say that the Gevaert patent specifications [5,6] allow for treatment with hydroxylamine above 100°C. and also simultaneous treatment and dyeing. In aqueous medium the reaction of hydroxylamine with polymers containing cyano groups leads to the intermediate formation of amidoxime groups, which are immediately converted into hydroxamic acid groups. Contrary to expectation, the improvement in dyeability of the treated fibres is due to the presence of hydroxamic acid groups, not to that of amino groups.

F. SCHOUTEDEN

GEVAERT PHOTO-PRODUCTEN NV.
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13th January 1959

[1] Khachoyan, J., and Niederhauser, J. P., J.S.D.C., **74**, 133 (1958); *Teintex*, **22**, 910 (1957).

[2] DuP, *USP* 2,653,074 (priority 24.5.1951, published 22.9.1953).

[3] CFM, *FP* 1,094,620 (priority Germany 18.12.1952).

[4] Pacific Mills, *USP* 2,792,276 (priority 18.1.1954, published 14.5.1957).

[5] Gevaert, *BP* 786,960 (priority United Kingdom 24.9.1954).

[6] Idem, *FP* 1,153,625 (priority United Kingdom 30.3.1955).

[7] CFM, D.A.S. [*German Application*] 1,024,484 (30.4.1955).

[8] Wagner, E., *DDP* 13,439 (priority German Democratic Republic 20.10.1955); *Deutsche Textiltechnik*, **7**, 145 (1957).

[9] Fran, *FP* 1,160,105 (26.10.1956).

[10] Schouteden, F., *28e Congresso Intern. Química Industrial*, **2**, 878 (Madrid, Oct. 1955).

[11] Idem, *Makromol. Chem.*, **24**, 25 (1957).

[12] Idem, *Chim. et Ind.*, **79**, 749 (1958).

[13] Idem, *Makromol. Chem.*, **27**, 246 (1958).

[14] Valentine, L., J.S.D.C., **74**, 138 (1958).

[15] Khachoyan and Niederhauser, *ibid.*, **74**, 135 (Table II) (1958).

[16] Khachoyan, *ibid.*, **74**, 138 (1958).

Textile Finishing in the Early 1900s

Those of my era, that is to say the members of the Society who were engaged in dyeing and finishing and allied industries in the early 1900s, are amazed at the progress made, for what was in those days their craft has now become a science. The advance is such that most of my age find it difficult to follow the "resonances" and "symbols" and so on now part and parcel of any discussion. I was apprenticed to an important and large dyehouse in those days, and only entered the dye and chemical trades later on.

I hope it may be of interest to junior colleagues if I report that I well remember mercerising up to 7,000–8,000 pieces per week, and when the sodium hydroxide (52°Tw.) liquor had a deepish shade of Bismarck Brown. This liquor was steaming at noon, and had reached about 45°C. at the end of the working day (6 a.m.–6 p.m.). Despite the coloration and the temperature variation during the working day or night turn, the mercerising effect was magnificent and is no better today. The reason for the excellent result and the temperature need not be discussed here.

In those days litmus and Congo papers and the "common sense" preached by Dr. C. M. Whittaker were just about the only auxiliaries available in a dyehouse, and pH was unknown. Expressions like "grams per litre" and "c.c. per litre" were not used, and would have been thought out of place in a works.

When souring-off after mercerising, it was professional to check the acidity of that liquor with the tongue. And strange as it may seem, I am not aware that we ruined our cotton goods in the "bleach liquor" (sodium hypochlorite) and bleaching process, whether aiming at a full or only a semi-bleach, the latter for subsequent dyeing to particularly bright colours.

There is no intention whatever on my part to deny the processing advances in use today, but this modest reminder may not be unimportant to those interested in the history of the industry.

We will wish to express our gratitude to those splendid craftsmen who passed on their experiences to us.

HERBERT À BRASSARD

136 GROVE HALL COURT
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LONDON N.W. 8

16th April 1959

ERRATA

A Century of Progress in the Synthesis of Dyes for Photography. L. G. S. Brooker and P. W. Vittum (J.S.D.C., **74**, 766 (1958))—In line 6 above formulae X—XII the numbering of the compound should be 2:**6**-dibromo-1:**5**-dihydroxynaphthalene.

Reactive Dyes. J. Wegmann (J.S.D.C., **75**, 231 (April 1959))— In line 10 of the abstract "IV" should be replaced by **cyanuric chloride**, and in line 14 "V" by **metanilic acid**.

Terylene Patents (J.S.D.C., **75**, 256 (May 1959))— The statement that an appeal has been lodged is **incorrect.**

Notes

Meetings of Council and Committees
May

Council— 6th

Finance and General Purposes— 26th

Publications— 12th

International Federation 1959 Congress—
Planning and Co-ordinating— 12th

Colour Index Editorial Board— 12th

Review of Textile Progress— 8th.

Dyed Flowers

According to *Industrial and Engineering Chemistry* (**51**, 33A–34A (March 1959)) J. R. Clopton at the University of Colorado is working out methods of preserving and colouring cut flowers which are being applied commercially on a large scale, e.g. to carnations, under the trademark Petalife. The solutions used contain a nutrient such as sucrose, a metabolic inhibitor such as quinol, and an antiseptic such as di-isobutylphenoxyethoxyethyldimethylbenzylammonium chloride. The colorant is a water-soluble anionic dye, which is sucked up the stem and into the petals. Since such a dye is not substantive to cellulose, it is deposited at the surface of the petals as the water evaporates, and gradually fills in the vessels within the petals. Fancy effects (e.g. coloration of the fringes of the petals only) are obtained by varying the rate of migration of the dye.

Among problems still to be solved are to make the vessel walls in the petals permeable to dye, so that uniform coloration can be achieved; and to use a black dye successfully, for at present the molecules of such dyes are too large to get into the petals, and dye mixtures would migrate at different rates.

OBITUARY NOTICE

Luigi Sessa

Dr. Luigi Sessa was born in Milan on 13th February 1887. The study of chemistry was something of a tradition in his family, and he devoted himself to it; in 1910, after a brilliantly successful university career in pure chemistry, he obtained his doctor's degree. Immediately on finishing his studies at Pavia he set up a consulting laboratory and quickly established himself as a leading figure in the Italian chemical industry.

In 1915 he was directing the Ballistics Laboratory of the Italian Armed Forces, and was given the direction of the Projectile Section of the Arsenal at Piacenza by the Italian High Command.

Immediately after the end of the First World War he took up work as chemical consultant to Lanificio Rossi and to Conservazione Legno e Distillerie Catrame S.p.A. (Cledca); on behalf of Lanificio Rossi he established in 1924 Industria Applicazioni Chimiche for the manufacture of dyes and textile auxiliary products, and remained a director of this concern for over thirty years. In 1938 he became president of Società Vernici Italiana Standard, and in 1948 director and then vice-president of Società Cledca.

Dr. Sessa devoted a great deal of his energy to questions of standardisation, and during the past ten years has given a strong impetus to this work by presiding over the meetings of the ISO/TC 47 (Chemistry) Committee, the secretariat of which is held by Italy.

In 1951 Dr. Sessa became President of the Associazione Italiana di Chimica Tessile e Coloristica and in 1956 President of the International Federation of Associations of Textile Chemists and Colourists. He relinquished this last position only a few months ago, and his last act in the organisation was his induction of the writer as President at the Milan meeting of the Council of Delegates.

Since 1955 Dr. Sessa has been President of the National Association of Chemical Industry in Italy. He was also Vice-president of the Industrial Association of Lombardy.

As a result of his work for the International Standards Organisation and the International Federation of Associations of Textile Chemists and Colourists, his participation in various international bodies, including the Technical Committee of the International Wool Textile Organisation, Luigi Sessa was one of the best known international figures in the field of textile dyeing and finishing. He was also one of the best loved. He was a man of great personal charm; his remarkable and diverse abilities and acute mind went with a quiet and modest manner which won him friends in all spheres of his work. What time he spared for private life Dr. Sessa devoted to his farm in Mirabello Ferrarese, which was equipped and run on the most modern lines.

It was partly because of his farming activities as well as for his great services to industry that in May 1958 Luigi Sessa was awarded the very high distinction of Cavaliere del Lavoro.

Dr. Sessa died in Milan on 14th March 1959, leaving a wife, a daughter, and three grandchildren.

JOHN BOULTON

New Books and Publications

Recent Progress in the Chemistry of Dyes and Pigments

(*Lectures, Monographs, and Reports 1958. No. 5*)

By W. Bradley. Pp. ii + 94. London: Royal Institute of Chemistry. Price, 9s. 0d.

In 1938 the late Professor F. M. Rowe contributed a well esteemed and oft quoted monograph, entitled *The Development of the Chemistry of Commercial Synthetic Dyes (1856–1938)*, to the Institute's series of monographs. In view of the wide scope of the progress that has been achieved during the last twenty years, the need has been felt for some time for an authoritative and up-to-date account of the chemistry of synthetic colouring matters. This demand is met by Professor W. Bradley's monograph, throughout which emphasis is placed on the chemistry of the dyes, treated concisely yet comprehensively in twelve main sections.

The first section (of 21 pages) is the largest and is devoted to the quinonoid colouring matters. The considerable progress made in this large and important group of dyes is well summarised.

Then come two sections dealing respectively with indigoid and thioindigoid dyes and with sulphuric esters of reduced forms of vat dyes.

Metal-containing dyes and pigments are then considered. These form one of the most important groups of colouring matters at the present time and one which is being most actively studied. Recent developments have been concerned mainly with the 2:1 dye–metal complexes and are described here.

In the next section, developments in the phthalocyanine field are described. These are concerned mainly with the preparation and use of a wide range of copper phthalocyanine derivatives.

This is followed by 17 pages devoted to the very large and still rapidly expanding azo class of dyes and pigments. An interesting account is given of developments in four subgroups. This section concludes with 4 pages dealing with advances in the general chemistry of azo compounds.

A short account follows next of anthraquinone dyes other than vat dyes, in which important technical progress has been made. Reference is made to the great variety of dyes belonging to this class which can be applied as disperse dyes to the hydrophobic fibres. A series of wool dyes that are resistant to severe washing is also referred to.

Triarylmethane dyes are then considered. A new development which concerns these dyes, in particular the basic dyes, is their suitability for the dyeing of polyacrylonitrile fibres. The author describes an interesting preparative method for basic triarylmethane dyes. Among other significant developments described are four new methods for the preparation of vinylogues of the triarylmethane dyes.

In an article on methin dyes, important advances are dealt with. These include the development of a new series of methin dyes, which are bright basic dyes and are particularly suitable for the printing of cellulose acetate.

Among the important advances in the dioxazine and azine dyes described here are developments concerned with colour photography and the production of oxidation blacks.

The next section, devoted to sulphur dyes, gives an account of recent work which has added somewhat to our limited knowledge of their chemistry.

Finally comes a section entitled "Other New Classes of Dyes", which the author deals with under the subheadings—reactive dyes, the Alcian dyes, fluorescent whitening agents, and synthetic carotenoids.

A list relating the molecular structures described to the common names of the dyes and their *Colour Index* numbers is included as an appendix, and ample references are given to original work.

As a lucid and concise exposition of the present state of knowledge concerning the chemistry of synthetic colouring matters, the monograph is to be highly recommended. J. T. CHAMBERLAIN

Reports on the Progress of Applied Chemistry Volume XLII: 1957

London: Society of Chemical Industry. [1958.] Pp. 910. Price, 100s. 0d.

This annual review requires no recommendation, nor is it even possible to give in the prescribed maximum space an appropriate and adequate account of its contents. The volume records many indications and results of further developments in research and production.

In the section on Intermediates and Dyes (C. H. Reece) there are tables of the U.S.A. production of coal-tar dyes by chemical and dyeing classes, and it is interesting to note that, for 1956, azo dyes (with 33·7% total by weight), sulphur dyes (21·2% total by weight), and anthraquinone vat dyes (19·1% total by weight) represent 74% of the U.S.A. production of coal-tar dyes. It would be of considerable interest if comparative figures for production and consumption of dyes in Britain were available and published (as the reviewer has mentioned before).

Among the changes in the manufacture of dye intermediates was an increase in the use of petroleum as a source of primary products, and further progress was made in azo and anthraquinone dyes, also in the range of phthalocyanine and chlorotriazine dyes with the Procion and Cibacron reactive dyes.

In the chapter on Cellulose Textile Chemistry the authors (N. S. Wooding and R. S. Mahomed) review the more important advances in dyeing technology and theory and chemical treatments for cellulosic fibres. Reference is made to new continuous dyeing methods including a technique for high-temperature fabric dyeing described by S. N. Bradshaw (*Man-made Textiles*, **33**, 73 (1956)), in which dyeing is carried out from molten urea at 140°C., and this method seems to be applicable to

tightly woven cotton or rayon fabrics, as well as to the dyeing of secondary cellulose acetate and cellulose triacetate with disperse dyes (the reviewer could not find any reference to this method in the *Review of Textile Progress* for 1957 or 1958). Further work has been published on the etherification and esterification of cellulose, on anti-soiling, and on "ease-of-care" finishes associated with new fibres.

Further progress has been made in the production of synthetic fibres, as shown by the reports by J. F. Lloyd Roberts on acrylic fibres, P. Markey on fibres from isotactic polymers, and F. K. Duxbury and J. E. McIntyre on polyamide and polyester fibres respectively. P. T. Speakman surveys developments in textile finishing, comprising scouring, bleaching, heat-setting, dyeing, moth-proofing (with Dieldrin), and resin finishing.

In the introduction to their report on detergents the authors (H. E. Garrett and T. G. Jones) show a tabulation of world soap–detergent consumption for 1954–1955; it is gratifying to note that, after the U.S.A. with an annual *per capita* consumption of 27·8 lb., Britain comes next with 24·3 lb., closely followed by Australia and New Zealand (23·1 lb.) and Canada (22·4 lb.), with India (0·6 lb.) and China (0·3 lb.) at the bottom of the list. There are also chapters on production, formulation, physical properties, mechanism of detergency, and new analytical test methods for detergents and surface-active products. To the many references the second edition of *Textile Chemicals and Auxiliaries* by H. C. Speel and E. W. K. Schwarz should be added.

Other sections in this volume relate to progress made in fuel and fuel products, metals, leather, antibiotics, plastics, adhesives, radioactive isotopes, and many other branches of physics and chemistry.

There are well compiled name and subject indexes at the end of the book, and many useful references to the literature and patents in the text.

A. F. KERTESS

Vorbehandlung und Färben von synthetischen Faserstoffen

By H. U. Schmidlin. Pp. viii + 358. Basle: Verlag Schweizerische Vereinigung von Färbereifachleuten. 1958. Price, Swiss francs 20.00.

As the author points out, there is a considerable volume of published, but widely dispersed, information on the pretreatment and dyeing of man-made fibres. The technical service departments of the manufacturers of both dyes and fibres are also far from inactive. Nevertheless, until this volume appeared, there was no single work in existence which the dyer could keep for handy reference. One can appreciate the difficulties of covering a rapidly developing field in which new fibres, dyes, and processes are appearing almost daily, and therefore all the more credit is due to the author for producing up-to-the-minute information and to the S.V.F. for undertaking publication.

The treatment is strictly practical. If some of the pages have the appearance of circulars, they are clear, and have not been lifted bodily from manufacturers' pattern cards. There has been a serious attempt to collate such information into tables which draw comparisons between the products available, factually and without bias.

The book commences with a review of the raw materials with which it deals in the form of a table of man-made fibres, which includes the name, the chemical constitution, and the manufacturer. The description of the preparatory processes then begins. This is not skimped, and desizing, scouring, and setting are covered in sufficient detail for the practical man to whom the book is addressed. Bleaching methods and the use of fluorescent brightening agents are next dealt with. There then follows a discussion with clear illustrations of the machinery used in the preparation, setting, and pressure-dyeing of man-made fibres. The treatment of the Barotor is extremely well done.

The main part of the book, dyeing, then follows. Each fibre is considered in turn after a general discussion on carriers and fastness properties. In this section topicality is very pronounced and recipes are given profusely. Nylons 6, 6,6, and 11, polyesters, polyacrylonitrile, mixed polymers, polyvinyl chloride, and cellulose triacetate are each discussed. This then develops into a discussion of the dyeing of mixtures, following roughly the same scheme as that adopted for the unmixed fibres.

The volume concludes with a useful section on continuous preparation and dyeing processes for man-made fibres, including resin-bonded pigment systems. This section is, perhaps, a little too brief, and the reader is left wanting more.

The print, paper, and binding make this book a pleasure to handle. The clear style of the author and the workmanlike index make it a must for every dyehouse handling man-made fibres and having a member with an acquaintance, however slight, with German. One could have wished for a loose-leaf format to allow for constant revision of the changing situation, but the book will probably sell out so rapidly that the second edition will not long be delayed.

S. R. COCKETT

Brushmaking Materials

By F. Kidd. Pp. xiv + 188 + 96 half-tone illustrations. London: British Brush Manufacturers Research Association. 1957.

This book, written by the Director of Research of the British Brush Manufacturers Research Association, will be found of great interest to the members of the Society who are interested in a field of work closely associated with the substrates of the dyeing industry.

The book is well supplied with excellent and interesting photomicrographs of the particular materials of all types used for brushes and of faults in brushes of various types. The accounts of brush-filling materials are concise and lucid, and cover those of animal, vegetable, and man-made origin, and in this respect constitute a poor man's "Matthews". Further chapters outline methods of

identification of, and the effect of moisture in, brush-filling materials, their physical and chemical properties, and a brief and interesting account of the processing of materials for brush fillings.

Finally, there are a technical account of adhesives, handles, backs, boards, stocks and quills, etc. as used in the make-up of brushes and a final discussion on damaged brushes and the care of brushes.

In all respects, this is a most readable booklet, well referenced throughout, so that anyone wishing for more detailed exposition of any section can readily go to the original source for information. It should be a valuable book on the shelves of all concerned with fibres. R. L. ELLIOTT

Elementary Practical Organic Chemistry

Part III—Quantitative Organic Analysis

By Arthur I. Vogel. Pp. xiii + 645–840 + i–xxxii. London: Longmans, Green & Co. Ltd. 1958. Price, 21s. 0d.

The previous two parts of Dr. Vogel's most valuable *Practical Organic Chemistry* were reviewed in this *Journal* for October 1957 (**73**, 466). It is therefore a great pleasure that we receive the third and final part of the present work, covering Quantitative Organic Analysis. This is a most excellent addition to the library of the laboratory, particularly for workers in industry, and even on occasions for research workers. It is an entirely new work and covers— determination of selected elements in organic compounds; general discussion of titrations in non-aqueous solvents; hydroxyl groups (alcohols); adjacent hydroxyl groups (polyhydric alcohols) and periodate titrations; hydroxyl groups (phenols); amino groups; salts of amines (including quaternary ammonium salts); amino acids; carboxyl groups and their salts, anhydrides, and esters; aldehydes and ketones; carbohydrates (sugars); nitro, nitroso, and azo groups and reduction with titanous salts; unsaturation; alkoxyl groups; *C*-methyl, *O*-acetyl, and *N*-acetyl groups; active hydrogen; enols; imides; sulphonamides, thiols, sulphides, and disulphides; determinations using ion-exchange resins; applications of the Karl Fischer reagent; α-epoxy groups (oxiran compounds); and in the last chapter a series of important determinations— formaldehyde, acetone, aromatic hydrazines, urea, peroxides, and isocyanates.

The methods all appear to be sound. Full details are given of the material and apparatus requirements. Without any doubt this will be found the most valuable of the three parts, and it can be firmly recommended. R. L. ELLIOTT

Organic Chemistry

Electronic Theory and Reaction Mechanism

By Rowland I. Reed and S. Horwood Tucker. Pp. viii + 108. London: Macmillan & Co. Ltd. 1956. Price, 15s. 0d.

The development of knowledge of and interest in reaction mechanisms of organic chemistry has resulted since the Second World War in a variety of books dealing with the detail of this subject, particularly those by Dewar and Ingold. Many members of this Society will have found these somewhat heavy reading, usually having only a vague memory of the fundamentals of the electronic theory of organic compounds and modern views on atomic and molecular structure. The present little book is obviously an attempt to present to such readers the basic principles of this modern study of reaction mechanisms, and the authors state their indebtedness to Ingold, Coulson, Palmer, Linus Pauling, Walsh, and Wheland for permission to incorporate quotations from their fuller theories on valency structure and mechanisms. The reviewer feels that the book does present in a readable form the essential details of the electronic theory. It can be easily read by anyone with a basic chemical knowledge, and with the corrections incorporated in the diagrams on pp. 32–38 (which are included in the review copy), there is no difficulty in understanding the intricacies of molecular orbitals. The subsequent chapters cover the intramolecular influence of atoms and groups on valence electrons; the physical methods of measurement; the physical evidence for conjugative electron shifts; interatomic (internuclear) distances; the hydrogen bond; and the very simplest exposition of the basic mechanisms of the simpler organic reactions such as addition and replacement. This last chapter, whilst comprising only eight pages, is quite adequate to indicate effectively that the work covered in the rest of the book is the essential groundwork for a more detailed study of reaction mechanisms. It is a pity that the authors did not eliminate from the list of electron donor and acceptor properties on p. 28 the confusing Lapworth nomenclature of "anionoid" and "cationoid", although it is known that one dye chemist of the Lapworth school still speaks publicly in these terms.

Certain misprints of single bonds occur on p. 46 but are self-evident. This book is recommended as a simple introduction for all anxious to keep themselves abreast of modern developments in the field of mechanisms and structures of complex organic molecules. R. L. ELLIOTT

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Continuous Scouring and Bleaching of Silk and Rayon Fabrics

R. V. En'kova *Tekstil. prom.*, **18**, 45–50 (Aug. 1958)

A multiple-box machine, VZhN–4–ShL, for continuous rope scouring and bleaching of natural silk, viscose rayon, and cellulose acetate fabrics is described in detail. The fabric is padded in caustic soda, sodium silicate, and hydrogen peroxide (total alkalinity 1·6–2·2 g./litre), steamed, and washed. Typical fabrics quoted are light rayon crêpe, heavy silk crêpe, and viscose/acetate union fabrics. Advantages claimed are speed of operation, retainment of full crêpe and handle, and absence of rope marks. G.J.K.

Automation in Bleaching

Ya. S. Zalmanzon, G. G. Zelenskaya, and V. N. Nebarov *Tekstil. prom.*, **18**, 43–45 (Aug. 1958)

The project of a fully automatic plant for cotton bleaching (alkaline peroxide) is reviewed in general terms. G.J.K.

Machine for the Impregnation of Cotton and Rayon Staple Fabrics with Azoic Coupling Components

N. V. Korol'kov *Tekstil. prom.*, **18**, 33–34 (Nov. 1958)

Heat-treatment Plant for Crease-resisting and Water-repellent Finishes

A. G. Antropov *Tekstil. prom.*, **18**, 39–40 (Oct. 1958)

PATENTS

Recovering Carbon Black (C.I. Pigment Black 6 and 7) from a Gaseous Suspension

Phillips Petroleum Co. *USP* 2,864,674

Apparatus in which a fluidised bed of Carbon Black pellets, replenished by recycled pellets from a pellet mill, is used to collect Carbon Black particles from a gas in which they are suspended. C.O.C.

Carbon Black Furnace Dual Fluid Injector

Phillips Petroleum Co. *USP* 2,864,673

Furnace Black (C.I. Pigment Black 6 and 7)

Phillips Petroleum Co. *USP* 2,865,717

Placing a choke of a critical size in a critical position in a conventional Carbon Black furnace results in the yield of pigment per gallon of hydrocarbon feed being maintained while the abrasion resistance of the pigment is much increased and its heat build up is much decreased. C.O.C.

Calcining Titanium Dioxide (C.I. Pigment White 6) and other Pigments

DuP *USP* 2,865,622

A method of introducing additional heat at the mid-portions of the kiln without encountering additional dust losses, overburning, contamination, chemical reduction, or excessive loss of heat. C.O.C.

Heating Thermoplastic Yarn during Processing

Universal Winding Co. *USP* 2,864,931

Apparatus for the electrical heating of thermoplastic yarn in conjunction with winding, twisting, dyeing, etc. C.O.C.

Spray Units for Washing Machines

F. Smith & Co. (Whitworth) *BP* 811,377

Means are described which enable the orifices of the sprays to be cleared without stopping the machine. C.O.C.

Automatic Regulation of the Continuous Application of Controlled Quantities of Solids or Liquids to a moving Cloth or other Sheet

British Cotton Industry Research Assocn. *BP* 811,795

The material to be applied is mixed or dissolved in a liquid in a stock tank. It is supplied to this tank at a rate predetermined by the rate of travel of the sheet and the weight of material to be applied. This tank forms part of a closed circulatory system of small capacity. Any deviation of the actual rate of application of the material from the prescribed rate of application affects the rate of flow from the tank. Change in the weight of liquid in the other part of the circulatory system caused by change in the rate of flow from the tank is used to alter the concentration of the solution or suspension being applied so as to correct the actual rate of application of the material. C.O.C.

Wet Processing of Knitted Fabric

Wolsey *BP* 811,369

Rinsing is effected continuously and quickly with much saving in the water required by lifting the roped or bunched fabric past a series of vertically spaced squeezing devices. The rinse water flows downward in contact with the fabric as it passes each squeezing device below the water inlet. The speed of lift of the fabric and the volume of rinse water supplied to the squeezing devices are such that all the liquid in the fibre, including residual liquid from any previous wet process, is squeezed out of the fabric, the purer rinse water treating that portion of the fabric which has already been partly rinsed. C.O.C.

Penetration of and Removal of Liquid and Gas from Permeable Materials

J. Zakarias and L. Zakarias *BP* 811,570

Safety Device for Squeeze Rollers

Bleachers' Assocn. *BP* 810,962

Modification of *BP* 749,325 (J.S.D.C., **72**, 384 (1956)), the device being much simplified by the detector being electroacoustic instead of electromechanical. C.O.C.

Continuous Wet Processing and Drying of Freshly Spun Rayon Filaments

W. H. Furness *BP* 811,272

A thread advancing reel of the common type is described on which the thread is wound in a series of superimposed alternately reversed helices, the helical disposition being produced solely by oscillation of the thread guide. This results in a tube of yarn being built up having a wall 0·25 in. thick, the tube being conveyed by the axial movement of the reel from one end to the other of the reel continuously. During this movement along the reel the yarn is wet processed and dried. This enables the wet processing of the yarn to be assisted by centrifugal force and drying to be carried out in absence of tension. The floor space required per thread or station is exceptionally small. C.O.C.

Beam Dyeing

Rhoden Dyeing Co. *BP* 810,673

A machine which winds the yarn on to the beam so that the tension in the yarn decreases linearly from a maximum at the core of the beam to a minimum at the outside of it. This prevents formation of air locks in the beam, channelling and slipping or compacting of the yarn during dyeing. C.O.C.

Heating Cloth, etc.

H. Krantz Sohne *BP* 810,564

An arrangement which ensures uniform distribution of the hot gas over all the nozzles of a drying machine or the like. C.O.C.

Screen for Textile Drying Machines

James Hunter Machine Co. *USP* 2,862,306

A screen for removing lint or other particles from the drying medium. It can be readily cleaned. C.O.C.

Size Box

Cocker Machine & Foundry Co. *USP* 2,862,280

Simple and cheap means for minimising temperature drop at the surface of the size. This prevents accumulation of solidified size on the rollers and other parts of the size box and slasher. C.O.C.

Drying of Knitted Garments or the Pre- or Post-boarding of Stockings

Samuel Pegg and Son *BP* 810,605

Apparatus in which carriages bearing the formers can be propelled from opposite ends so that they can be periodically interchanged in the heating chamber. The cycle of interchange of the carriers in the chamber and supply of hot gas to the former and movement of the carriages are carried out in automatic sequence. C.O.C.

Laterally Guiding Travelling Webs of Paper
K. Warner-Jones & Co. *BP* 811,574
Apparatus for effecting lateral alignment register of the paper comprises a vacuum tension element extending across the width of the paper and in contact with it and means for varying the degree of vacuum along the element so as to vary the tension across the paper. C.O.C.

Continuous Screen Printing
Münchner Modedruck Weishäupl & Co. *BP* 812,000
The necessity for using an adhesive to secure the cloth to the rubber belt used as the printing table is removed if the cloth is led over a uniformly upwardly inclined and then downwardly inclined support above which are placed the screens. Thus the rubber belt supporting the cloth may run over an upwardly arched table or rotatable cylinder. As a result of this arching the cloth is safely held in position without an adhesive and satisfactory registration is obtained. C.O.C.

Treating Polyethylene Film or the like to High Voltage Electrical Discharge
Celanese Corpn. of America *BP* 811,370
Simple apparatus is described in which a film is subjected to a diffuse high voltage electrical discharge without any danger of the dielectric material which has to be placed between the electrodes becoming buckled or distorted and so coming into contact with the film and scratching it. C.O.C.

Applying Films to a Base Sheet
Meyercord Co. *BP* 811,537
A machine for applying transfers to sheet material by the use of heat and pressure. C.O.C.

Heating of Thermoplastic Synthetic Materials (XIII p. 340)

II— WATER AND EFFLUENTS

PATENT

Treating Water to prevent Scale Formation
Sta-lit Lighter Co. *USP* 2,864,750
Exposure of water to immersed electrodes, neither of which are consumed during their working, each selected for specific ampere hour effects such as O_2 adsorption and its reduction to hydroxyl ions, increased alkalinity about one electrode and film resistance to electric current flow at one electrode, not only prevents scale forming but results in scale already present being gradually removed. C.O.C.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Infrared Spectra and Solvent Effects
II— Carbonyl Compounds
L. J. Bellamy and R. L. Williams
Trans. Faraday Soc., **55**, 14–18 (Jan. 1959)
Carbonyl frequency shifts of a wide range of compounds in many solvents appear to be produced by local association effects and not by dielectric constant factors. The sensitivities of carbonyl groups to solvent effects have been measured and the significance of the results is discussed.

III— Intermolecular and Intramolecular Hydrogen Bonds
L. J. Bellamy and H. E. Hallam
Ibid., 220–224 (Feb. 1959)
Effects of solvents on stretching frequencies of inter- and intramolecular hydrogen bonds have been studied. Results confirm that solvent shifts are due to local interactions with solvent. W.R.M.

Adsorption at the Surface of Dilute Soap Solutions
S. A. Flengas and E. Rideal
Trans. Faraday Soc., **55**, 339–349 (Feb. 1959)
Radioactive tracer and other studies of sodium stearate solutions indicate that the Gibbs adsorption equation is not applicable to dilute soap solutions in conductivity-water. At higher concentrations the results indicate surface association of solute. W.R.M.

Decomposition of Anionic Surface-active Agents by Soil Bacteria
F. A. Skinner *Nature*, **183**, 548–549 (21 Feb. 1959)

PATENTS

Detergent
Thomas Hedley & Co. *BP* 811,902
Addition of a compound of formula $R^1R^2N{\cdot}CO{\cdot}NR^3R^4$ (one of R^1, R^2, R^3, R^4 = Alk of 10–15 C, another = a monosaccharide or reducing oligosaccharide radical, and the remainder = same or different, H or Alk of 1–3 C which may be substituted by 1 or more OH groups), e.g. *N*-dodecyl-urea-*N'*-glucoside, to organic anionic sulphate or sulphonate detergents, imparts good lathering properties. C.O.C.

Detergents
Fettchemie VEB *BP* 811,732
A detergent suitable for all types of fabric comprises a buffer mixture containing an alkali metal bicarbonate and a neutral washing composition in which an aqueous solution has pH 7–7·5 at 30–40°C. and 8·5–10·0 at 70–100°C. and which at 70–100°C. gives off CO_2. C.O.C.

Detergents for Materials containing Wool and/or Nylon
Phillips Petroleum Co. *USP* 2,864,866
Compounds of formula $R{\cdot}SO{\cdot}(CH_2CH_2{\cdot}O)_nH$ (R = n-Alk of 12–16 C or t-Alk of 14–16 C; n = 4–7) e.g. 14-hydroxy-3,6,9,12-tetraoxatetradecyl t-tetradecyl sulphoxide, are colourless, colour-stable, almost odourless detergents for wool and nylon. C.O.C.

Improving the Foaming Properties of Anionic Sulphated Synthetic Detergents
California Research Corpn. *USP* 2,863,836
The foaming performance of sulphate detergents containing a straight saturated C_{14}–C_{18} hydrocarbon chain is much enhanced by addition of a blend of 3–0·3 parts of a *p*-acyl phenoxy compound and 1 part of a fatty acid amide, e.g. *p*-acyl phenoxy ethanol (acyl from coconut fatty acids) and myristamide. C.O.C.

Surface-active Materials
Shawinigan Chemicals *BP* 811,693
Highly effective surface-active agents are obtained by treating acrylic acid, methacrylic acid, an alkyl (Alk of < 11 C) acrylate or methacrylate, or methacrylonitrile with SO_3 and an organic peroxy compound. The strongly acid products are oil-soluble emulsifying and stabilising agents, particularly for vinyl acetate and acrylic esters. C.O.C.

Wetting Agents
Sun Oil Co. *USP* 2,860,143
Cyclic sulphonic acids are incompletely oxidised to produce additional carboxyl acidity in the sulphuric acid molecules. Their nitrogen base salts have very powerful wetting properties. C.O.C.

Increasing the Detergent and Lathering Properties of Alkyl Sulphuric Acid Ester Salts
Thomas Hedley & Co. *BP* 810,688
Addition of high molecular alkyl esters of *p*-hydroxybenzoic acid, e.g. dodecyl *p*-hydroxybenzoate, improves the detergent and lathering properties of compositions based on high molecular alkyl sulphuric acid ester salts, e.g. sodium dodecylbenzene sulphonate. C.O.C.

Coloured Detergent
Henkel and Cie. *BP* 811,028
It has become commercially desirable to colour detergents without the colour being imparted to textiles washed with them. This can be achieved by incorporating an oxygen-yielding substance, e.g. a per-compound, in the detergent and using a dye which is at least partly decolorised by oxidation during normal use of the detergent, e.g. C.I. 73015 and 73020. C.O.C.

Tallow Emulsions
E. Mercer *BP* 810,383
Stable emulsions of tallow are obtained by mixing tallow with a sulphated fatty alcohol of 9–18 C and either a fatty acid of 16–18 C, e.g. stearic acid, or a mineral oil, heating to melt the tallow and then adding with constant stirring hot water containing enough alkali to neutralise the free fatty acid in the mixture. The addition of the hot water should be done at a speed intermediate between that which would cause frothing and that which would cause the mixture to become lumpy. C.O.C.

Products Containing Polymerised *N*-Vinyl Lactams and Polyalkylene Imines—Textile Assistants, Coating Agents, etc.
BASF *BP* 811,135

A mixture of a polymer prepared from a *N*-vinyl lactam, if desired together with another polymerisable compound, and a polyalkylene imine is, in presence of water or an organic solvent (preferably one miscible with water), allowed to stand for some time and/or heated and/or the solvent eliminated by evaporation or *in vacuo*. The products have very wide uses including *inter alia* as auxiliary agents in the processing of textiles, binding agents, adhesives, coating agents. They can be prepared on a substrate, thus cloth is coated with an alcoholic solution of polyvinyl caprolactam and then with polyethylene imine followed by calendering, steaming or infrared irradiation. C.O.C.

Basic Vinyl Polymers for Improving the Fastness of Direct Dyes
BASF *USP* 2,861,863

The wet fastness of direct dyeings on cellulosic materials is much improved by treating them with polymers containing basic groups and free from carbonyl groups, e.g. the quaternary ammonium compound obtained from poly-*N*-vinyl-2-methylolimidazol and *p*-toluene sulphonic methyl ester. C.O.C.

Alkoxy Aluminium Chelates—Water Repellent Agents
DuP *BP* 811,125

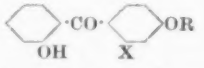
Compounds of average formula $Al(R^1)_x(OR^2)_y$ (R^1 = anion from a bidentate chelating agent having an alkyl chain of > 11 C and an acidic H atom, being attached to the Al through at least one O atom; R^2 = Alk of 1–4 C; x and y are each $\leqslant 0{\cdot}5$ but total 3) are obtained by a cyclisation reaction in which the acidic H group in the chelating agent reacts with one alkoxy group in the aluminium trialkoxide to form an alcohol, the reaction concluding with chelate formation. Thus octadecyl acetoacetate refluxed with aluminium isopropoxide in benzene yields an oily product of formula $C_{28}H_{55}O_5Al$. These aluminium chelates have wide application in reducing the water-permeability of porous substances and in producing water-repellent coatings. They are used preferably as dispersions or solutions in organic solvents. C.O.C.

Fur Glazing Composition
W. C. Ware *USP* 2,861,949

An aqueous dispersion of a dialkyl dimethyl ammonium salt, a silicone oil and a tertiary amine or a polyalkylene ether of an alkylated phenol when sprayed on to a fur not only glazes the fur but also makes it smooth and soft and resistant to soiling. One such dispersion consists of a 75% solution of dialkyl dimethyl ammonium chloride in isopropanol (2 oz.) (Alk from soya fatty acid), polydimethyl siloxane (1 oz.), condensate of 1 mol. nonyl alcohol with 10 mol. ethylene oxide (1 oz.) and water to make 1 gal. C.O.C.

Ultraviolet Radiation Absorbing Agents
American Cyanamid Co. *BP* 810,570

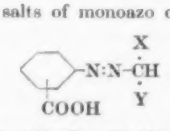
Compounds of formula—



(X = H or OH; R = Alk, subst. Alk, aralkyl, or alkenyl), e.g. 2,2′-dihydroxy-4-methoxybenzophenone, are excellent absorbers of ultraviolet radiation which can be readily made into molecular dispersions in various organic carriers. They are resistant to the conditions of curing of plastics. C.O.C.

Monoazo Ultraviolet Radiation Absorbing Agents
ICI *BP* 811,113

Divalent metal salts of monoazo compounds—



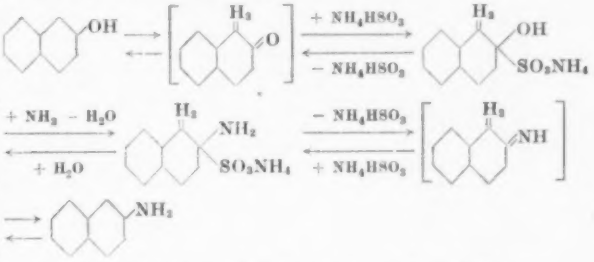
(X and Y = CN, CO·CH_3, CO·NH_2, or COOAlk; the benzene ring may contain substituents such as Hal, CN, SO_2Alk, COOAlk, COOH, etc.) absorb little visible light, but absorb strongly in the ultraviolet region without being strongly fluorescent, and are suitable for incorporating in varnishes and synthetic polymer wrapping materials to give protection from ultraviolet radiation. Thus diazotised anthranilic acid is coupled with diethyl malonate, and the product converted into its Ba salt, which is a yellow powder. E.S.

Tertiary Amine Oxides—Vat Printing Auxiliaries (IX p. 330)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Studies in the Naphthalene Series. XVIII—Kinetics of the Reaction of β-Naphthol with Ammonia and Ammoniumbisulphite
V. V. Kozlov and I. K. Veselovskaya
Zhur. obshch. khim., **28**, 3333–3338 (Dec. 1958)

The kinetic investigation of the Bucherer reaction has confirmed the schematic representation shown below—



The investigation shows that the reaction is dependent on bisulphite but independent of ammonia concn. G.J.K.

Substitution Reactions with 2-Methoxy- and 2-Ethoxy-1-naphthylamines
F. Bell *J.C.S.*, 519–525 (Feb. 1959)

Whereas chlorination and nitration proceed mainly, or even exclusively, in position 4 of the acetyl, formyl, and toluene-*p*-sulphonyl deriv. of 2-methoxy- and 2-ethoxy-1-naphthylamine, yet bromination may yield the 6-deriv. as the main product, e.g. with the *N*-acetyl-2-methoxy- and *N*-acetyl-2-ethoxy-1-naphthylamine. The bromination of 2-methoxy- and 2-ethoxy-*N*-formyl-1-naphthylamine, however, afford the 4-deriv. as the only readily isolable cpd., although 2-ethoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine give the 4-deriv. as the main product with ~ 20% of the 6-deriv. A comparison is made with the results of substitution experiments with 2,6-xylidine. H.H.H.

Polynitronaphthalenes. II—Quantitative Study of the Nitration of 1- and 2-Nitronaphthalene and of 1,5-Dinitronaphthalene
E. R. Ward, C. D. Johnson, and L. A. Day
J.C.S., 487–493 (Feb. 1959)

Methods are described for the application of column and paper chromatography, and complex formation, to the detection, separation, and estimation of products arising from the nitration of 1- and 2-nitronaphthalene and of 1,5-dinitronaphthalene. The influence of nitration medium, temp., and added catalyst has been studied in appropriate cases, and discussed in relation to current theories of aromatic nitration, particularly the dipolar influences of the nitro-group (the D-effect of Ward and Wells, cf. *Chem. and Ind.*, 1172 (1958)).

1,3,5,7-Tetranitronaphthalene is found to be a nitration product of 1,5-dinitronaphthalene, and improved and convenient preparative methods are described for 1,3,5- and 1,4,5-trinitro- and for 1,3,5,8-, 1,3,5,7-, and 1,4,5,8-tetranitro*naphthalene*. The latter may be prepared directly from 1-nitronaphthalene. H.H.H.

Preparation of *o*-Nitrosophenol from Salicylic Acid
A. A. Nemodruk
Zhur. obshch. khim., **28**, 2672–2676 (Oct. 1958)

A new and interesting method for the preparation of *o*-nitrosophenol from readily available materials is described. Salicylic acid is reacted with sodium nitrite in the presence of acetic acid and divalent copper salts. The

presence of the copper salt allows complex formation with the *o*-nitrosophenol preventing further reaction of the latter with nitrous acid. This method is noteworthy for the high yield obtained. G.J.K.

Oxygen Exchange between Nitrous Acid and Water
C. A. Bunton, D. R. Llewellyn, and G. Stedman
J.C.S., 568–573 (Feb. 1959)

The rate of exchange of oxygen atoms between water and nitrous acid is proportional to the square of the nitrous acid concn., and this corresponds to the formation of N_2O_3 with consequent oxygen exchange. The rate of formation of N_2O_3, estimated from the rate of oxygen exchange, is similar to that estimated from the rate of diazotisation of aniline. H.H.H.

Replacement of Halogen in Azo Compounds

IV— Replacement of Chlorine in 5-Methyl-2-chlorophenylazo-2′-naphthol by Alkoxy and Aryloxy Groups and the Preparation of Simple Ethers of 3-Amino-4-hydroxytoluene
B. I. Stepanov
Zhur. obshch. khim., **28**, 2676–2682 (Oct. 1958)

The azo dye prepared from diazotised 3-amino-4-chlorotoluene and alkaline β-naphthol is reacted in the presence of copper salt with either sodium alcoholate or sodium phenolate, when replacement of the chlorine atom by alkoxy or aryloxy group, respectively, occurs. The following groups have been introduced in the form of simple ethers (R = C_2H_5; n-C_4H_9; iso-C_5H_{11}; n-C_6H_{13}; n-C_8H_{17}; n-$C_{18}H_{37}$; C_6H_5-CH_2; β-C_5H_9-C_2H_4; γ-C_6H_5-C_3H_6; C_6H_5; and other phenyl derivatives). Reaction is carried out successfully in an inert solvent (toluene or xylene). The reductive fission of the alkoxy- or aryloxy-substituted dyes produces simple ethers of 3-amino-4-hydroxytoluene.

V— Interaction of the Copper Complex of 2-Chlorophenylazo-β-naphthol with Alkoxides
M. A. Andreeva and B. I. Stepanov
Ibid., 2966–2967 (Nov. 1958)

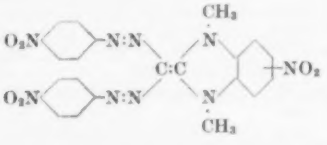
The interaction of the copper complex of the azo dye from 2-chloroaniline and β-naphthol with the sodium salt of either n-butyl or benzyl alcohol in the corresponding alcohol as solvent allows the quantitative replacement of the chlorine atom by the butoxy and phenylmethoxy groups respectively.

VI— Replacement of Chlorine by Methoxyl in 2-Hydroxy-8′-chloro-(1,1′)-azonaphthalene and in its Copper Complex
B. I. Stepanov and V. A. Savel'ev *Ibid.*, 2968–2971

The interaction of sodium methoxide with 2-hydroxy-8′-chloro-(1,1′)-azonaphthalene (I) in the presence of copper salt allows a quantitative replacement of chlorine by the methoxyl group under mild conditions (heating by means of a water bath with a mixture of toluene and methanol as solvent). It is shown that the halogen atom in the *peri* position (8′) possesses the same mobility as that in *o*-chloro-*o*′-hydroxy-azo compounds. A copper complex of I has been prepared and treatment of this complex with sodium methoxide causes replacement of the halogen atom by the methoxyl group.
G.J.K.

Azo Dyes derived from 2-Methylbenziminazole
N. T. Le Bris and H. Wahl
Rev. textile-tiba, **57**, 164–171 (1958): *Chem. Abs.*, **53**, 2208 (10 Feb. 1959)

Methylation of a mixture of 5- and 6-nitro-2-methylbenzimidazole (I), or nitration of 1,2-dimethylbenzimidazole, gives mixtures of the 5- and 6-nitro-1,2,3-trimethyl derivative, which couples with diazotised *p*-nitroaniline to give the disazo dye—



The corresponding monoazo dye was prepared by condensing the aldehyde, prepared by oxidation of I, with *p*-nitrophenylhydrazine. E.S.

Metal-complex (Monoazo) Dyes
A. Trzaszczka-Krasuska
Przemysl Chem., **35**, 332–336 (1956) (English summary): *Chem. Abs.*, **53**, 3699 (25 Feb. 1959)

Preparations of Co and Cr complexes of monoazo dyes obtained by coupling diazotised 2-aminophenol-4-sulphonamide with β-naphthol, 1-acetamido-7-naphthol, 3-methyl-1-phenyl-5-pyrazolone and acetoacet-*o*-chloroanilide are described. E.S.

Malachite Green-reducing Enzyme in *Mycobacteria*
I. Tárnok and P. Czanik
Nature, **183**, 549–550 (21 Feb. 1959)

Photoreduction of Methylene Blue (C.I. Basic Blue 9)
C. A. Parker *J. Phys. Chem.*, **63**, 30–34 (Jan. 1959)

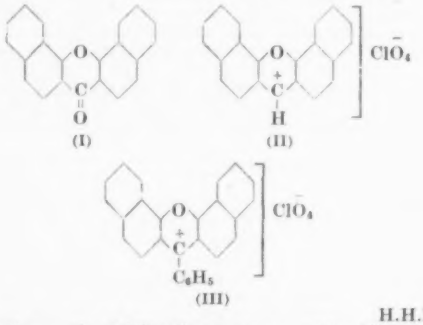
Dilute solutions of methylene blue in dilute sulphuric acid are reversibly bleached by flash photolysis giving two transient species. These are tentatively identified and results discussed in relation to the slow reoxidation of leuco Methylene Blue. W.R.M.

Photoionisation of some *p*-Substituted Triphenylmethane Leuco Cyanides
E. O. Holmes *J. Phys. Chem.*, **62**, 884 (1958): *Chem. Abs.*, **52**, 19505 (25 Nov. 1958)

The absorbencies of the carbonium ions produced by photoionisation of the leuco cyanides dissolved in 1,2-dichloroethane do not offer a good basis for comparing the effects of the various groups substituted in the *para* position. A better basis would be the degree of photoionisation. C.O.C.

Dibenzoxanthylium Salts
M. Kamel *Helv. chim. Acta*, **42**, 580–582 (March 1959)

A simple method is described for preparing 3,4,5,6-dibenzoxanthone (I) by heating 1-hydroxy-2-naphthoic acid for 30 min. at 300°c., following which come the syntheses from I of 3,4,5,6-dibenzo- (II) and 9-phenyl-3,4,5,6-dibenzo- (III) xanthylium perchlorate—



H.H.H.

Reaction of 2-Nitrofluorenone with Potassium Hydroxide, Aniline, and Sodium Anilide
W. Bradley and F. P. Williams
J.C.S., 1205–1211 (March 1959)

Previous work (cf. *J.C.S*, 1254 (1932) and 360 (1959) on the direct replacement of hydrogen in nitrobenzene and α-nitronaphthalene by amines is now extended to 2-nitrofluorenone. With KOH in pyridine, 2-nitrofluorenone gives 3-hydroxy-2-nitrofluorenone and a dicarboxylic acid of 4,4′-azoxydiphenyl, and with aniline and KOH, the products are 6-hydroxyquinoxalino-[2,3-*a*]fluorenone and a 4-phenylazodiphenylcarboxylic acid. Sodium anilide with 2-nitrofluorenone at 20°c. gives the anil of 2-phenylazofluorenone, also prepared from 2-aminofluorenone. At 40–45°c. sodium anilide produces two cpd. $C_{24}H_{15}N_3$ and $C_{24}H_{13}ON_3$, considered to be the anil of 13-oxofluoreno-[1,2-*b*]quinoxaline and a related monoxide of this. 13-Oxofluoreno[2,3-*b*]quinoxaline is prepared for comparison. The mechanism of the reactions involved is discussed. H.H.H.

Primary Photoprocesses in Quinones and Dyes
N. K. Bridge and G. Porter

I— Spectroscopic Detection of Intermediates
Proc. Roy. Soc., **A 244**, 259–275 (1958)

In flash photolysis of quinones in solution, appearance of intermediates is related to the efficiency of the quinone as a photosensitiser. Transient spectra were studied for duroquinone as a function of solvent and pH. The solvents

used were paraffin, hexane, 3-methylpentane, cyclohexane, $CHCl_3$, CCl_4, ether, dioxan, and ethanol. Studies were also made with naphthoquinone, anthraquinone and 2-methylanthraquinone. With a variety of quinones there is marked tendency to form the semiquinone radical by H abstraction and for this radical to exist in its relatively stable radical ion form at high pH and in its unchanged form at low pH. The triplet state was never observed for very long and was only evident in viscous solvents with duroquinone.

II— Kinetic Studies *Ibid.*, 276–288
Chem. Abs., **52**, 19504 (25 Nov. 1958)

Kinetic studies for the semiquinone radical, the radical ion and the triplet state of duroquinone in paraffin and aqueous alcohol, but no definite conclusions can yet be drawn about the relationship between the structure of a dye and its sensitising properties. C.O.C.

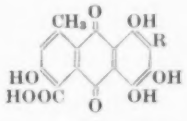
Syntheses of 4-Iodoalizarin-3-Sulphonic Acid and of 4-^{131}Iodoalizarin-3-sulphonic Acid
M. Frankel and P. Moses
Chem. and Ind., 401–402 (21 March 1959)

The initial material, 4-aminoalizarin, is conveniently made by the catalytic hydrogenation of 4-nitroalizarin in ethanol using 30% Pd–charcoal as catalyst, following which it is sulphonated to 4-aminoalizarin-3-sulphonic acid (I) by heating with oleum (10 parts) at 135° c. for 45–75 min. I is then converted to 4-iodoalizarin-3-sulphonic acid (II) by the usual diazotisation–KI procedure with suitable experimental modifications.

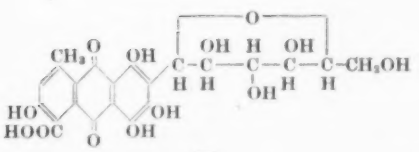
II is converted into 4-^{131}iodoalizarin-3-sulphonic acid—(*a*) by treating its soln. in KOH containing KI with one of carrier-free radioactive iodine at a concn. of 2·27 μcurie per ml. for 24 hr., the resulting radioactive material giving 10,000 counts/mg. on the Geiger counter, indicating a radioactive exchange of the order of 0·8–1·6%; and (*b*) from the diazonium salt soln. of I above, by treatment with aq. KI and a soln. containing ^{131}iodine at a concn. of 1·9 μcurie/ml., when the resulting product afforded 30,000 counts/mg. H.H.H.

***C*-Glycosyl Compounds. III— Carminic Acid**
M. A. Ali and L. J. Haynes
J.C.S., 1033–1035 (March 1959)

Carminic acid, which was given the structure (I) by Dimroth and Kamerer (*Ber.*, **53**, 471 (1920)) where R = $C_6H_{11}O_5$, is now shown to be the *C*-glucopyranosyl cpd. (II) by ozonolysis to give arabinose, and by periodate oxidation of methyl carminate tetramethyl ether, which at 0° c. consumed 2·1 mol. of periodate with formation of formic acid.



(I)

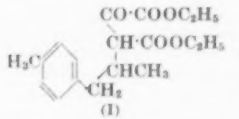


(II)

H.H.H.

β-Aroylpropionic Acids
IX— Their Conversion into 1,2-Benzanthraquinones
F. G. Baddar, I. M. Dwidar, and M. Gindy
J.C.S., 1001–1009 (March 1959)

The ester (I) cyclises with 75% v/v H_2SO_4 to 3,4-dihydro-3,7-dimethylnaphthalene-1,2-dicarboxylic anhydride, which dehydrogenates to 3,7-dimethylnaphthalene-1,2-dicarboxylic anhydride, and this with arylmagnesium halides gives a mixture of 1- and 2-aroyl-3,7-dimethyl-2- and -1-naphthoic acid. The latter are separated, reduced to the corresponding benzylnaphthoic acids, cyclised, and finally oxidised to the corresponding 1,2-benzanthraquinones.



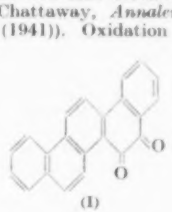
(I)

X— Conversion of γ-Aryl-β-phenylbutyrates into Polynuclear Compounds
F. G. Baddar, A. M. Fleifel, and S. Sherif
Ibid., 1009–1012

Reduced β-benzoyl-β-phenyl- and β-phenyl-β-*p*-toluoylpropionic acids are converted into 2,3-benzofluorenones, which are alkali fused and the resulting acids recyclised to the corresponding 1,2-benzofluorenones. H.H.H.

Synthesis of Polycyclic Aromatic Compounds. II— Picene-5,6- and -13,14-quinone and Picene-5,6,7,8-diquinone
W. Davies and B. C. Ennis
J.C.S., 915–918 (March 1959)

The synthesis of polycyclic quinones, and thence of their parent aromatic hydrocarbons, by the Diels–Alder reaction of *p*-quinones with 1-vinylnaphthalene and related dienes (cf. *J.C.S.* 4967 (1957)), is now extended to the synthetic use of *o*-quinones. 1-Vinylnaphthalene and 3-bromo-1,2-naphthaquinone are found to yield picene-5,6-quinone (I), which, together with a smaller amount of picene-13,14-quinone, is now separated from the "picene quinone" of obscure structure described in the literature (Bamberger and Chattaway, *Annalen*, **284**, 52 (1895); Cook, *J.C.S.*, 685 (1941)). Oxidation of I gives picene-5,6,7,8-diquinone.



(I)

H.H.H.

Non-crystallising Phthalocyanine Pigments
Y. Banshō, S. Suzuki, and I. Saito
Rept. Govt. Chem. Ind. Research Inst. Tokyo, **53**, 325–329 (xxxvii-xxxviii) (Sept. 1958)

Solvent-stable blue-tone copper phthalocyanine powders having good pigment properties have been prepared, and the following experimental results obtained—(1) Non-crystallising phthalocyanine pigments were obtained by mixing Fe, Al, Ti, Mg, and Sn phthalocyanine with Cu phthalocyanine. (2) When Fe, Al, Mg, Cr, and Sn phthalocyanines were used, the required light fastness (Fade-O-Meter) was not obtained. (3) When Fe, Al, Ti, Ni, and Cr phthalocyanines were mixed with Cu phthalocyanine, the colour of the products became greenish blue in a printing varnish, and generally the pigments thus produced became more greenish than the original Cu phthalocyanines. (4) When the products were boiled in xylene or toluene, the tinting strengths of the mixed pigments containing Zn or Fe phthalocyanines did not change, those containing Al, Ti, Cr, and Co phthalocyanines decreased to some extent, and those containing other phthalocyanines decreased as the ratios of mixing increased. (5) Some demetallisation occurred when the metal phthalocyanines were mixed in sulphuric acid. They were mixed only mechanically in this experiment. C.J.W.H.

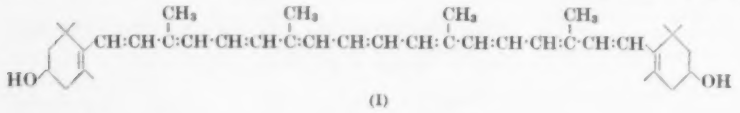
Carotenoid Syntheses
XXVI— Introduction of Mercapto and Anilido Groups into β-Carotene
C. Martin and P. Karrer
Helv. chim. Acta, **42**, 464–466 (March 1959)

The reaction of *N*-bromosuccinimide with β-carotene in the presence of phenylmercaptan yields 4,4′-di-phenylmercapto)-β-carotene, and, similarly, in the presence of aniline or *N*-methylaniline, it gives 4,4′-dianilido- or 4,4′-di(*N*-methylanilido)-β-carotene respectively.

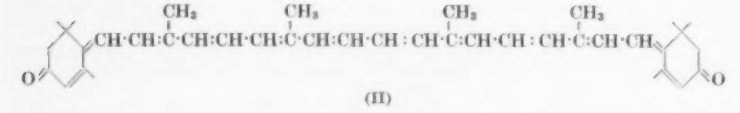
XXVII— Synthesis of Rhodoxanthin, Retrodehydrokryptoxanthone, and Transformation Products of β-Carotenone
R. Entschel and P. Karrer *Ibid.*, 466–472

Zeaxanthin (I) is directly dehydrogenated by MnO_2 to give rhodoxanthin (II), and similarly kryptoxanthin is

converted into the monoketone retro-dehydro-kryptoxanthin. β-Carotenone is reduced by aluminium isopropoxide to a tetraol and thence dehydrogenated by MnO_2 to a dioldione and also to a triolone, each having the same carbon structure as β-carotenone.



(I)



(II)

H.H.H.

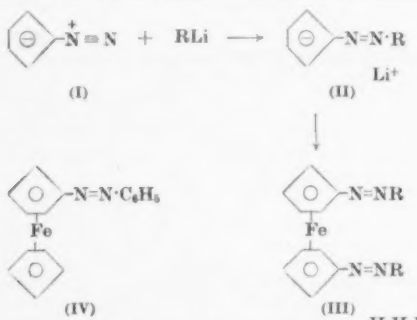
Structures of Spirilloxanthin and Related Carotenoids

M. S. Barber, L. M. Jackman, and B. C. L. Weedon
Proc. Chem. Soc., 96–97 (March 1959)

Azoferrocenes

G. R. Knox *Proc. Chem. Soc.*, 56–57 (Feb. 1959)

Hitherto, azoferrocenes have remained inaccessible, but it has now been found that when phenyl- or methyl-lithium reacts with diazocyclopentadiene (I) in ether, a dark red cpd. is formed (presumably the salt (II)), which with anhyd. $FeCl_3$ gives the desired products, viz., black 1,1′-diphenyl- and maroon 1,1′-dimethyl-azoferrocene (III: R = C_6H_5 or CH_3), in good yield. Violet monophenylazoferrocene (IV) is obtained by adding cyclopentadienyl-lithium to II, and treating the mixture with anhyd. $FeCl_3$. The parent aminoferrocenes and their simple deriv. are readily obtained from the azoferrocenes



(I) (II) (IV) (III)

H.H.H.

Colour Isomerism and Structure of some Copper Co-ordination Compounds

T. N. Waters and D. Hall

I— Absorption Spectra in Solution

J.C.S., 1200–1203 (March 1959)

Significant differences in the electronic absorption spectra from 200 to 800 mμ. of some copper(II) complexes of salicylaldehyde and 2-hydroxy-1-naphthaldehyde deriv. in pyridine, methanol, benzene, chloroform, and carbon tetrachloride, suggest that the colour of the green isomers is due to a five- or six-fold co-ordination of the copper atom, in contrast to the violet or brown isomers, where only four-fold co-ordination is indicated. Measurements at 0°, 25°, and 43°c. afford no evidence of a temp. effect.

II— Absorption Spectra of Solids *Ibid.*, 1203–1205

For comparison purposes with I, the electronic absorption spectra of the solid copper (II) complexes above are obtained for potassium bromide discs. From the data, it is evident that the green complexes have a metal co-ordination number > 4. H.H.H.

Polycyclic Aromatic Hydrocarbons in Carbon Blacks

A. J. Lindsay, M. A. Phillips, and D. S. Wilkinson
Chem. and Ind., 1365–1366 (18 Oct. 1958)

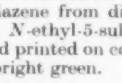
An American sample of carbon black which had been specially prepared by solvent treatment for the printing industry did not contain polycyclic hydrocarbons. Two European samples contained the carcinogenic hydrocarbons 3,4-benzpyrene 1% and 1,2-benzpyrene 0·2%, together with pyrene 1·7%, fluoranthrene 1·1%, acenaphthene 0·5–1%, and lesser amounts of seven other hydrocarbons. One sample also contained 5·8% anthracene. Identifications are based on spectral analysis of the fractions obtained by chromatography on alumina.
E.V.T.

PATENTS

Phthalocyanine Acid Amides— Coupling Components for Azoic Greens

FBy *BP* 811,221

Acid halides of phthalocyanine carboxylic and sulphonic acids are condensed with amines of the naphthol, arylpyrazolone, or acylacetarylide series to give sulphon- and carbon-amides



(Pc = phthalocyanine residue; R^1 = SO_2 or CO; R^2 = residue of an amino-naphthol, -arylpyrazolone, or -acylacetarylide linked to R^1 by the amino group; R^3 = NH_2 or an organic amine linked to R^1 by the amino group and not containing a group which directs coupling; m and $m + n$ = integers from 1 to 4; SO_3H and COOH groups are absent). Thus copper phthalocyanine-(3)-trisulphonyl chloride is heated in chlorobenzene at 90–95°c. with 1-*p*-aminophenyl-3-methyl-5-pyrazolone.

BP 811,222

The phthalocyaninesulphonamides described in *BP* 811,221 above couple on cellulose with suitable diazo compounds to give mainly bright green azoic dyeings and prints. Thus the condensation product of copper phthalocyanine-(3)-trisulphonyl chloride with 1-*p*-aminophenyl-3-methyl-5-pyrazolone is dissolved in aq. NaOH, mixed with 3 mol. of the triazene from diazotised 2-amino-4,5-dichlorotoluene and *N*-ethyl-5-sulphoanthranilic acid, suitably thickened, and printed on cotton. Neutral or acid steaming produces a bright green. E.S.

Diazotisation of Weakly Basic Amines

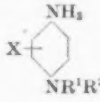
FBy *BP* 809,350

Weakly basic amines of low solubility in water can be successfully diazotised under quite weakly acid conditions (pH 5–1·5) if their particle size is first reduced below about 10 μ. by grinding with suitable dispersing agents. Thus a 26% paste of 4-amino-2,5-dimethoxy-4′-nitroazobenzene (1050) and a condensation product (500) of formaldehyde with naphthalenesulphonic acid are dispersed in a kneading apparatus to an average particle size of 3 μ. After dilution, diazotisation with acetic acid and sodium nitrite at pH 2·9–3·5 gives nearly 100% yield. E.S.

Colour Developers

Agfa *BP* 811,679

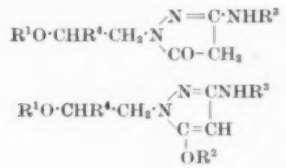
Compounds of formula—



(R^1 = Alk of 3–4 C; R^2 = ω-sulpho-*n*-propyl or -butyl (the propyl may be substituted by methyl); X = H, Alk or alkoxy; the total number of C atoms in the alkyl radicals attached to the tertiary N atom must be > 6), e.g. 4-(*N*-n-butyl-*N*-ω-sulpho-n-butylamino)-aniline, enables dye components to be used which previously had very limited or no application because of their low coupling power, but which were particularly valuable for building up a multi-colour image because of their step absorption flanks, e.g. indazolone components. The dye images produced with these developers are faster to light than those produced e.g. with diethyl-*p*-phenylene diamine. They have the further advantage of not staining the skin of anyone working with them. C.O.C.

3-Acylamido-5-pyrazolone and 3-Amido-5-acyloxy-pyrazole Colour Couplers
Eastman Kodak Co. *USP* 2,865,748

Compounds of formula—

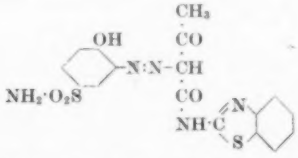


and

(R^1 = H or acyl; R^2 and R^3 = acyl; R^4 = H, Alk or monocyclic Ar), e.g. 1-(β-hydroxyethyl)-3-[α-(p-palmitamidophenoxy) - acetamido] - 5 - pyrazolone, yield with primary aromatic developers magenta dyes having a wider range of light absorption than those obtained from previously known pyrazolone and pyrazole couplers. This makes them suitable for use with benzoyl acetoalkoxyanilide yellow dye-forming couplers in multilayer colour photography. C.O.C.

Yellow and Orange Metal-complex Monoazo Dyes for Wool from Acetoacetamido-benzthiazoles and -carbazoles
Fran *BP* 810,207

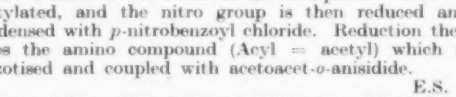
The 1:2 metal-complexes of monoazo compounds obtained by coupling diazotised o-aminophenols or anthranilic acid, which may carry non-solubilising substituents (especially $SO_2{\cdot}NH_2$), with acetoacetamidobenzthiazoles and -carbazoles dye wool, nylon, etc. yellow or orange from neutral or weakly acid baths. Thus diazotised 2-aminophenol-4-sulphonamide is coupled with 2-acetoacetamidobenzthiazole to give



Refluxing with aq. sodium cobalto-tartrate gives the cobalt-complex which dyes wool yellow. E.S.

Greenish-yellow Dischargeable Monoazo Stilbene Direct Dyes
Ciba *BP* 810,297

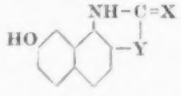
N-*p*-Aminobenzoyl derivatives of diaminostilbenedisulphonic acid



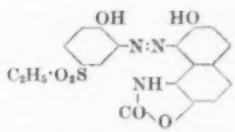
(Acyl = preferably acetyl or benzoyl) are diazotised and coupled with acetoacetarylides to give the title dyes. Thus 4-amino-4′-nitrostilbene-2,2′-disulphonic acid is acetylated, and the nitro group is then reduced and condensed with p-nitrobenzoyl chloride. Reduction then gives the amino compound (Acyl = acetyl) which is diazotised and coupled with acetoacet-o-anisidide. E.S.

Blue and Grey Metal-complex Monoazo Wool Dyes from 7′-Hydroxynaphthazoles
Gy *BP* 810,745

Anthranilic acid or o-aminophenol and their derivatives free of COOH and SO_3H groups are diazotised and coupled with 7′-hydroxynaphthazoles



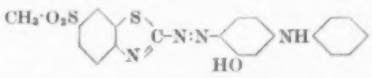
(X = O or S; Y = O or NH) and the monoazo compounds converted into Co and Cr complexes, which dye wool blue and grey. Thus diazotised 2-amino-4-ethylsulphonylphenol is coupled with 7′-hydroxynaphtho-1′,2′:4,5-oxazolone in presence of aq. NaOH and pyridine to give



Heating with aq. ammonium disalicylato chromate gives the Cr-complex which dyes wool blue-grey from a neutral or weakly acid bath. E.S.

Metallisable Benzthiazole Monoazo Disperse Dyes
Eastman Kodak Co. *USP* 2,857,371

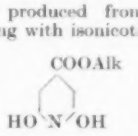
2-Aminobenzthiazoles, which may carry non-solubilising substituents, are diazotised and coupled with 3-hydroxy- or 3-alkoxy-diphenylamines to give disperse dyes which may be metallised, especially with zinc thiocyanate, on cellulose acetate. Thus 2-amino-6-methylsulphonyl benzthiazole is diazotised and coupled with 3-hydroxydiphenylamine to give



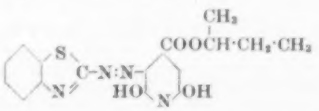
which dyes cellulose acetate red, converted to violet of improved wash fastness by padding with nickel thiocyanate and steaming for 15–20 min.

USP 2,857,372

Similar dyes are produced from the same diazo compounds by coupling with isonicotinic acid derivatives



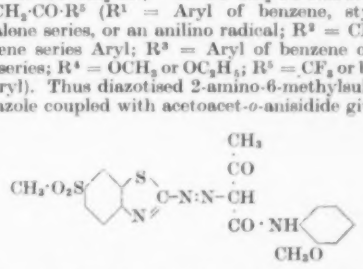
(Alk has 1–4 C). Thus diazotised 2-aminobenzthiazole with sec. butyl citrazinate gives



which dyes cellulose acetate orange, converted to bright bluish red by padding with nickel thiocyanate followed by steaming.

USP 2,857,373

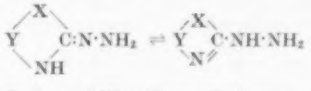
Similar dyes are given by coupling the same diazo compounds with the compounds having reactive methylene groups $R^1{\cdot}CO{\cdot}CH_2{\cdot}CN$, $R^2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}R^3$, and $R^4{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R^5$ (R^1 = Aryl of benzene, styryl, or naphthalene series, or an anilino radical; R^2 = CH_3, CF_3, or benzene series Aryl; R^3 = Aryl of benzene or naphthalene series; R^4 = OCH_3 or OC_2H_5; R^5 = CF_3 or benzene-series Aryl). Thus diazotised 2-amino-6-methylsulphonylbenzthiazole coupled with acetoacet-o-anisidide gives



which dyes cellulose acetate yellow improved in intensity and wash fastness by steaming with nickel thiocyanate. E.S.

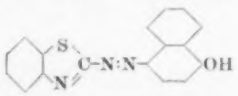
Heterocyclic Monoazo Dyes by Oxidative Coupling of a Hydrazine and a Coupling Component
BASF *BP* 810,736

Heterocyclic hydrazines of tautomeric formula—



(X = e.g. O, S, or $CAlk_2$; Y = ethylene or Alk- or Ar-subst. ethylene, o-phenylene, or o-naphthylene) combine with phenolic and amino coupling components in presence of oxidising agents to give azo compounds. Thus

2-hydrazinobenzthiazole (or benzthiazolone hydrazone) and α-naphthol dissolved in aq. ammoniacal methanol are treated at 30°c. with potassium ferricyanide to give

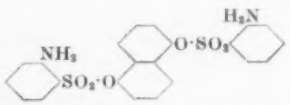


E.S.

Disazo Acid Dyes from Bis-sulphonic Acid Esters

FBy *BP* 810,246

Aromatic or araliphatic dihydroxy compounds are esterified with 2 mol. of nitrobenzenesulphonyl chlorides, and the products reduced to give diamines, which are tetrazotised and coupled with naphthylaminesulphonic acids or aminonaphtholsulphonic acids to give the title dyes. Thus 1,5-dihydroxynaphthalene esterified with *o*-nitrobenzenesulphonyl chloride and reduced gives the diamine

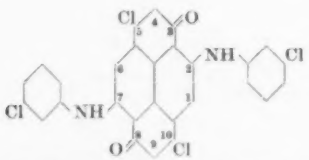


which is tetrazotised and coupled with 2 mol. of γ-acid in presence of acetic acid to give a bluish red. E.S.

Finely Dispersed Pyrenequinone Vat Dye

FH *BP* 810,980

2,7 - Di - *m* - chloranilido - 5,10 - dichloropyrene - 3,8 - quinone—



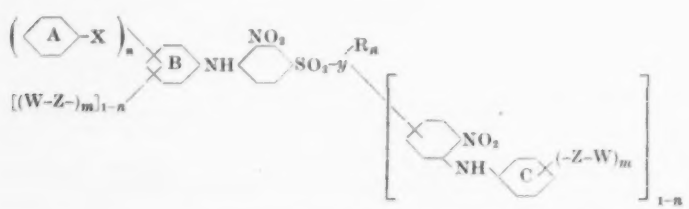
is a vat dye giving clear yellowish-green dyeings of excellent fastness but which are weak because the dye is extremely crystalline and difficult to vat. Normal pasting methods to improve its properties fail; e.g. (1) H_2SO_4, $ClSO_3H$ etc. treatments cause chemical changes; (2) ball milling with or without dispersing agents is ineffective; (3) vatting is slow and prolonged vatting removes Cl from the molecule. However, excellent results are obtained by dissolving the dye (12) in 96% H_2SO_4 (140) and glacial acetic acid (27) at 0°c. and stirring at 0–5°c. for 3 hr. The dye sulphate precipitates in very fine form on standing and decomposition of the sulphate is brought about by adding ice/water (500). Filtration and washing follow.

E.T.

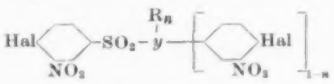
Diphenylamine Dyes for the Mass Coloration of Synthetic Fibres

S *BP* 810,360

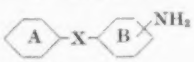
Yellow diphenylamine dyes of good solubility in organic solvents are



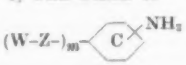
(*y* = a direct linkage, O, N, NH or NAlk when $n = 1$; or *y* = a direct linkage when $n = 0$; R = mono- or di-nuclear carbocyclic radical, aliphatic radical of 5–18 C or, when *y* is N and has mol.wt. < 91, a heterocyclic radical; X = direct C link, methylene, ethylene, vinylene, O, S, SO, SO_2, azo or oxymethylene bridge; Z = CH_2O, OCH_2O, $O(CH_2)_2O$, $O(CH_2)_3O$, $OCH_2CH(CH_3)O$ or $OCH(CH_2)CH_2O$; W = H or Alk which may have ether and/or OH groups; $m = 1$ or 2; $n = 0$ or 1. Nuclei A, B, and C may have further substituents. They are made by condensing



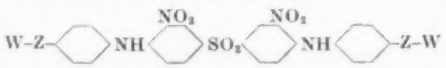
either (a), when $n = 1$, with 1 mol. of



or (b), when $n = 0$, with 2 mol. of



Acid-binding media are used in the condensations and water, ethanol, benzene, toluene, etc. are suitable solvents. Dyes of especial interest are of formula—

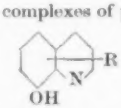


The coloured products of mass dyeing are fast to light, washing, cross dyeing, gas fumes, dry-cleaning, and peroxide. Dyeings from aq. dispersions result in unsatisfactory build-up. 75 examples are cited. E.T.

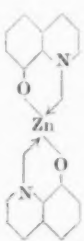
Fluorescent Paramagnetic Pigments

J. L. Switzer, R. C. Switzer, R. A. Ward, and J. D. Steele *USP* 2,864,771

The inner metallic complexes of phenols of formula—



(R = H or substituent) are condensed on a solid paramagnetic substrate so that molecular attraction exists between the complex and the substrate. Thus concentrated alcoholic solutions of $ZnCl_2$ and 8-hydroxyquinoline respectively are mixed and then red magnetic iron oxide, ground to an impalpable powder, is stirred in. KOH dissolved in 50% aqueous ethyl alcohol is then slowly added to the suspension with constant stirring. This results in the complex



being precipitated on the iron oxide. The resulting pigment is washed, ground, and dried. It is red-brown with bright yellow-green fluorescence under ultraviolet radiation. Its magnetic permeability is not less than that of iron oxide. C.O.C.

Chlorination of Metal-free Phthalocyanine

General Aniline *BP* 809,498

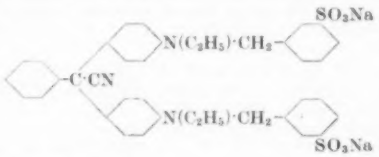
Earlier methods for chlorinating metal-free phthalocyanine $(C_8H_4N_2)_4H_2$, have serious disadvantages. Thus, high temperature is needed and solvent recovery is difficult as, e.g. when using molten phthalic anhydride or phthalyl chloride/$ZnCl_2$ as solvents; autoclaves are required, e.g. with Cl_2 in CCl_4 and Sb_2S_3 or with Cl_2 and S_2Cl_2; or special equipment not ordinarily used in chlorination is necessary as in the fluidised bed method. The present method employs Cl_2 and SO_2 at atmospheric pressure and at reflux temperature (195–200°c.) with trichlorobenzene as solvent and with addition of Sb_2S_3.

Chlorination to a Cl content of 46·6–47·5% gives a yellowish-green dye suitable for lacquers, paints, plastics, etc. E.T.

Hydrophilic Dye Cyanides

L. Chalkley *USP* 2,864,751–2

p-Amino triphenylmethane dye cyanides containing at least one hydrophilic group have hydrophilic properties and the same potential ultraviolet sensitivity possessed by the known hydrophobic dye cyanides. Unlike the hydrophobic *p*-aminotriphenylacetonitriles these hydrophilic cyanides, e.g. the cyanide of C.I. 42085—



are activated by water alone. C.O.C.

Cyanide of Soluble Blue (C.I. 42755)—Use in Photocopying Paper

L. Chalkley *USP* 2,864,753

Paper sensitised with the cyanide of C.I. 42755 when exposed to light prints out directly to yield images matching blue prints in hue and needing no further processing. C.O.C.

Pyrrocoline Disperse Dyes

American Cyanamid Co. *USP* 2,863,714

The arylides of 2,3-phthaloylpyrrocoline-1-carboxylic acids are disperse dyes which yield on polyester and cellulose acetate fibres dyeings of very good fastness to light and washing. Thus the anilide of 2,3-phthaloylpyrrocoline-1-carboxylic acid dyes Dacron and cellulose acetate fibres lavender. They may be prepared e.g. by treating an acid chloride of a 2,3-phthaloylpyrrocoline-1-carboxylic acid with an aromatic amine, variation in the substituent on the amide group resulting in products of different hues being obtained. C.O.C.

Phthalocyanine Pigments Resistant to Flocculation

DuP *USP* 2,861,005

The tendency of a phthalocyanine pigment to flocculate is prevented by treating it so that $\geq 15\%$ of the molecules are substituted by the group $-SO_2NX_2$ (X = H, subst. or unsubst. Alk or Ar). Thus the pigment obtained by heating phthalic anhydride (121 g.), 4-chlorophthalic acid (32), 4(*NN*-diethyl)sulphamylphthalic acid (6·4), urea (222), $CuCl_2$ (44), NH_4 molybdate (6·3), deodorised kerosene (800 ml.) in 3 hr. to 195°C. and keeping at that temperature under reflux for 4 hr. has high tinctorial strength and excellent resistance to flocculation in lacquer vehicles. About 10% of the molecules contain the $-SO_2N(C_2H_5)_2$ group. C.O.C.

Phthalocyanine Pigments

American Cyanamid Co. *USP* 2,855,403

Phthalocyanine pigments which are non-flocculating and non-crystallising are made by reacting metal-containing or metal-free phthalocyanines and metal-containing or metal-free phthalocyanines containing Hal atoms or 0–1 SO_3H and 0·01–2 aminomethyl groups as substituents with a nitrogenous base having ≤ 2 H atoms on the basic N atom. Suitable aminomethyl substituents are phthalimidomethyl and *o*-carboxybenzamidomethyl; the nitrogenous base is selected from—NH_3 or primary aliphatic amines, e.g. saturated or unsaturated alkylamines, hydroxyalkylamines, alkylenediamines, arylalkylamines, etc. Thus, Cu phthalocyanine (100), methylolphthalimide (39) in 100% H_2SO_4 (1375) are heated at 80°C. to complete reaction. Separation after adding xylene sulphonic acid (260) by drowning into ice/water, filtering and drying gives a product containing an average of one phthalimidomethyl group per phthalocyanine mol. which exhibits severe flocculation by the test given in *USP* 2,327,472. If, however, the above product, before drying, is slurried with water (1000) containing 68% ethylenediamine (100) and heated at the boil, a non-flocculating product showing no shade change or loss of strength when heated in toluene (600 hr. 130°F.) is obtained. E.T.

Bz-1:Bz-1'-Dibenzanthronyls and their Derivatives

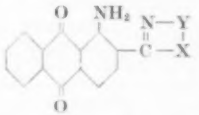
General Aniline *BP* 810,878

Earlier production methods comprise (1) heating benzanthrone with conc. H_2SO_4 and an oxidising agent, e.g. MnO_2; (2) as for (1) but using milder conditions thus leaving 30–40% of unchanged benzanthrone (*USP* 2,001,063); (3) using methyl or ethyl sulphuric acid instead of H_2SO_4 (*USP* 2,413,507). All give yields of $< 70\%$ whilst (2) and (3) involve extra treatments. The present method consists of condensing benzanthrone (with or without Hal, methyl or ethyl substituents) in a mixture containing conc. H_2SO_4, nitrobenzene (or its methyl, ethyl, propyl or butyl deriv.) and an oxidising agent, usually MnO_2. Yields are 75–95% and re-crystallisation or alk. extraction is unnecessary. Nitration of the condensation product may follow without intermediate separation. E.T.

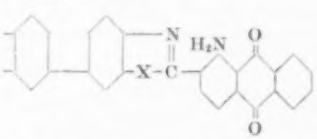
Thiazole and Oxazole Vat Dyes

FBy *BP* 811,386

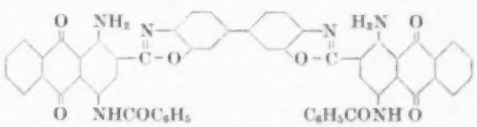
Vat dyes of high colour strength giving blue-violet to grey dyeings of good fastness are



(X = O or S; Y = *o*-phenylene, *o*-naphthylene, *o*-anthraquinonylene or the radical



≤ 1 Cl or acylamino substituent is present in one or both of the aminoanthraquinone mols.). For example

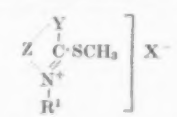


They are made by reacting subst. 1-aminoanthraquinone-2-aldehydes or their anils with *o*-aminophenols or *o*-aminothiophenols to give *o*-hydroxy- or *o*-mercapto-azomethines. Dehydrocyclisation of these compounds with oxidising compounds and alkaline agents, e.g. nitrobenzene and K acetate at 150–215°C., produces the final vat dyes. As the aminoanthraquinone-aldehydes are only obtainable with difficulty, it is better to start from the aldehyde-anils which are readily produced by reacting subst. 1-amino-2-methylanthraquinones with nitrobenzene at elevated temperature in presence of alkali and aniline (cf. *BP* 750,977). E.T.

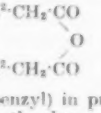
Symmetrical Monomethin Cyanine Dyes

Gevaert *BP* 811,156

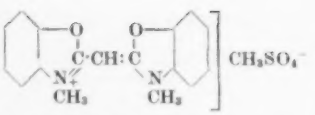
A 2-methylmercapto quaternary salt of an azole or hydrogenated azole base of formula—



(Y = O, S or Se; R^1 = Alk, alkenyl or Ar; X = anion; Z = atoms to complete a 5-membered heterocyclic nucleus) is condensed with an anhydride of formula—



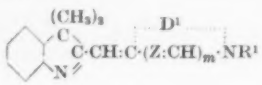
(R^2 = H, Alk, Ar or benzyl) in presence of an alkaline condensing agent. Thus the dye



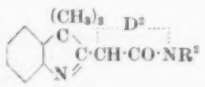
is obtained by refluxing 2-methylmercaptobenzoxazol dimethylsulphate with acetic anhydride in presence of triethylamine. C.O.C.

Cyanine Dyes
Ilford *BP* 811,876

Dyes of formula—



or



(R^1 = Alk or OH; R^2 = Alk, subst. or unsubst. Ar, or aralkyl; m = 0 or 1; D^1 = residue of a 5- or 6-membered ring; D^2 = atoms to complete a ketomethylene nucleus) have photosensitising properties. Thus the yellow dye 2 - (2,3 - dihydro - 3 - methyl - 2 - benzthiazolylidene) - methyl-3,3-dimethylindolenine obtained by fusing together 3,3-dimethyl-2-methylthioindolenine and 2-methylbenzthiazole metho-*p*-toluene sulphonate extends the sensitivity of a silver chloride emulsion to 4750 A. C.O.C.

Water-dispersible Carotenoid Compositions
Hoffmann-La Roche *USP* 2,861,891

A supersaturated solution of a carotenoid, e.g. β-carotene (C.I. Natural Yellow 26), is formed at 100–160°C. in an edible oil, e.g. coconut or cottonseed oil, and is rapidly emulsified with a 50% solution of gelatin in water. A concentrated aqueous solution of sugar is then added, the finished emulsion diluted to spray viscosity, e.g. 20–40% solids, with water and then sprayed into a collecting powder, e.g. starch, so that the droplets are kept separate from one another until they set as dry beadlets. Alternatively the emulsion may be spray dried. The products are used as food colours. C.O.C.

Isolating High Colour Polymers from Caramelised Sugar
Union Starch & Refining Co. *BP* 811,545

Caramelised carbohydrate solution containing caramel colour bodies, residual uncaramelised sugar or the fermentation inhibiting constituents formed when sugar is caramelised is treated to remove the fermentation inhibitors. It is then inoculated with an organism or enzyme which converts uncaramellised sugar to an organic material other than a carbohydrate, which material is then removed from the caramel colour bodies. The fermentation inhibitors may be removed by any method which does not affect the caramel colour bodies, e.g. by diluting with water and then concentrating under vacuum which results in the inhibitors also being evaporated off. Suitable agents for converting the unchanged sugar are *Aspergillus niger*, *Saccharomyces cerevisiae* (yeast) and *Bacterium putidum* which convert the sugar to citric acid, ethyl alcohol and CO_2, and gluconic acid, respectively. C.O.C.

Stabilised Copper Bronze Powders (C.I. Pigment Metal 2)
Sherwin-Williams Co. *USP* 2,864,719

Copper bronze when treated with a water-insoluble long chain aliphatic or alicyclic hydrocarbon acid of 8–32 C, e.g. stearic acid, and a water-insoluble rosin amine, is given improved stability when incorporated into coating compositions particularly in cellulose nitrate lacquers. The amount of the acid used is 0·5–5·0% and of the rosin amine 0·5–10·0% on the weight of the pigment. The pigment may be treated either before or shortly after its incorporation in the lacquer. C.O.C.

Nacreous Pigment from Glass
Francis Earle Laboratories *USP* 2,863,783

Glass platelets of length < 100 μ. and whose thickness is less than one quarter of their length, used as a suspension in a lacquer or other liquid which on solidifying has a refractive index < 88% of that of the glass, are an excellent substitute for Pearl Essence. C.O.C.

Calcination of Gypsum (C.I. Pigment White 25)
National Gypsum Co. *BP* 811,246

Gypsum ground so that 85% of the particles are < 150 μ. is continuously fed to the first of a series of elongated heating zones and then successively through each of the others. The mechanical feed acts within the body of the mass of gypsum which it indirectly heats. Additional heat is supplied indirectly to the gypsum from stationary heaters unconnected with the mechanical feed. As the gypsum is at no time in contact with the products of combustion of the heating medium a product of excellent purity of colour is obtained. C.O.C.

Dyes for the Mass Coloration of Cellulose (VIII p. 329)
Fast to Light Yellow to Orange Dyeings on Polyesters with Disperse Dyes (VIII p. 330)
Disperse Dyeing of Polyesters (VIII p. 330)
Dyeing Polyacrylonitrile Fibres with Basic Dyes (VIII p. 330)
Printing Wool with Insoluble Reactive Dyes (IX p. 331)
Fluorescent Brightening Agent for use in Photographic Paper or Emulsions (IX p. 332)
Fast Dyeing of Glove and Garment Leathers (XII p. 338)

V— PAINTS; ENAMELS; INKS

Fundamental Factors determining Coating Colour Viscosities— A Progress Report
V. F. Mattson and J. R. Leighton
TAPPI, **42**, 1–5 (Jan. 1959)

Laboratory coating colours were prepared by using portions of KCS clay slips. Pastes with solids contents between 8–30% were made by cooking starch suspensions for 10 min. at 87·5–93°C. in stainless steel beakers. Solids content, high shear viscosities and densities were measured. The fact that Robinson's equation is applicable to simple starch–clay coating colours containing 50–65% solids and 12–20% starch, implies they are suspensions whose specific viscosities are directly proportional to the volume concentration of pigment and inversely proportional to the volume of free liquid which in turn is related to the packed sediment volume of the dispersed pigment. R.A.

PATENTS

Pigmented Methyl Methacrylate Polymer Coating Compositions
DuP *USP* 2,860,110

Incorporation of a very small amount of cellulose nitrate, propionate, butyrate, acetate butyrate or acetate propionate into the composition results in it yielding dry films which have uniform pigmentation and absence of flooding, mottling or similar faults caused by poor dispersion of the pigment. C.O.C.

Pigmented Coating Compositions
ICI *BP* 811,502

Dimethylphthalate is added to an aqueous polymer dispersion of any type and then the pigment is added. The amount of phthalate used is 5–50% on the weight of the polymer in the dispersion. The use of the phthalate assists in the integration of the dispersed polymer particles in the film-forming process. Thus films formed from these compositions are rapidly and fully integrated and so possess superior drying properties and durability. Water paints based upon such compositions have a high standard of water and wet abrasion resistance in the early stages of drying. The phthalate also assists in the incorporation of any plasticiser present into the polymer particles. C.O.C.

Curing Coatings of Butadiene–Styrene Copolymer
Esso Research and Engineering Co. *BP* 811,903

Hard and glossy films are obtained without any discoloration by subjecting the coating to high intensity ionising radiation. C.O.C.

Cement Base Paint Compositions of Improved Miscibility with Water
Associated Portland Cement Manufacturers *BP* 812,086

The ease of wetting and dispersion in water of dry cement base paint compositions containing water repellent

materials is greatly improved by addition to the composition of an aliphatic monohydric alcohol of 6–10 C.
C.O.C.

Transfer Paper, Typewriter Ribbons, etc.
Gunther Wagner *BP* 810,401

The coloured products obtained by the action of acids on spiro-dipyrans, because of their high colour value and simplicity of formation, are exceptionally suitable for producing transfer papers, etc. which can be handled without dirtying the hands or papers in contact with it. They may be used in many ways. Thus a 0·3% solution of spiro-dibenzopyran in chlorodiphenyl (1 part by weight) is dispersed in 20% aqueous gelatose (5) and an acid-reacting paper is coated with this emulsion. Pressure on the coated paper causes a coloured mark. In another application typewriter ribbon is saturated with spiro-dipyrans and is then used in conjunction with acid reacting paper.
C.O.C.

Expanded Bead or Popcorn Type Stoved Finish
Midland Chemical Corpn. *USP* 2,862,834

Beads of a heat-expansible plastic are incorporated into a "force-dry" or stoving coating composition. When the product is applied and heated the plastic expands or "pops" like popcorn, to yield a film whose surface is composed of a multitude of closely packed expanded beads.
C.O.C.

Polycyclic Aromatic Hydrocarbons in Carbon Blacks (IV p. 320)

Stabilised Copper Bronze Powders (C.I. Pigment Metal 2) (IV p. 324)

Hectograph Process and Solvent (IX p. 331)

Condensates of Epoxidised Fatty Esters with Amine Compounds (XIII p. 340)

VI— FIBRES; YARNS; FABRICS

Bonded-fibre Fabrics
C. E. Coke *Chem. and Ind.*, 1569–1576 (29 Nov. 1958)

The development of bonded-fibre fabrics in the U.S.A. is reviewed (19 references). The earlier types, developed from 1946, were based mainly on cotton and viscose rayon fibres bonded with starch, glue, gums, polyvinyl acetate or cellulose (via the xanthate) and were of low quality. Introduction of a blend of 75% nylon–25% rayon and cotton bonded with butadiene–acrylonitrile rubber latex gave fabrics of good quality with excellent resilience. These proved suitable for garment interlinings although more costly than woven linings. The use of viscose rayon, cellulose acetate, special polyesters, polyacrylonitrile, and glass fibres followed, and fabrics based on these are available in the U.S.A., where the estimated 1957 production totalled 40,000 tons or 1·5% of total U.S. fibre usage.

Production involves opening, carding, laying, and bonding. Carding employs conventional machinery for the preparation of parallel- and cross-laid webs, but random-laid webs entail air deposition of fibres on a perforated drum operating under slight vacuum. Webs containing thermoplastic fibres or powder binders are bonded between hot rolls.

Liquid binders are the most common, and include solutions of water-soluble polymers such as glue or cellulose xanthate and dispersions of polymers (latices) such as polyvinyl acetate or butadiene–acrylonitrile copolymers. When applied by impregnation with the web carried between two fine-wire-mesh conveyor belts or between such a belt and a perforated drum, dense continuously bonded fabrics are obtained. When applied by printing or spraying, softer and bulkier fabrics are produced. Careful drying is necessary when liquid binders are used, and a curing stage may also be required, e.g. with rubber binders. Coloured fabrics are obtained by using coloured fibres, by pigmenting the binder, or by dyeing the finished fabric. A wide variety of finishing treatments are employed.

Properties of the ideal binder are considered in terms of strength, site of deposition, adhesion to fibre, and elastic recovery. Bonded fabrics are used in the U.S.A. in garment interlinings, air filters, leathercloth backing, wallpapers, and thermal insulation.
E.C.

Moisture Regain of Tightly Woven Cotton Fabrics
E. L. Skau and E. Honold
Text. Research J., **29**, 96–97 (Jan. 1959)

The results of moisture regain tests carried out on pieces of tightly woven material and yarns from similar pieces are presented and discussed. It is concluded that the compression of the fibres in the material prevents them from swelling freely and, therefore, limits the amount of water they can sorb.
S.B.D.

Fibre Structure and Mechanical Properties of Untreated and Modified Cotton
R. S. Orr, L. B. DeLuca, A. W. Burgis, and J. N. Grant
Text. Research J., **29**, 144–150 (Feb. 1959)

A brief review of investigations relating fibre structure to mechanical properties of cotton is given. The relationship of fibril arrangement, as measured by the X-ray technique, to the strength and elongation properties of cottons covering a wide range in physical properties is discussed. Alteration of mechanical properties of cotton brought about by degradation in hydrochloric acid, mercerisation, decrystallisation in ethylamine, resin treatment, and acetylation are related to changes in the fibre structure. The effects of stresses imposed during some treatments are discussed.
S.B.D.

Effect of Mercerisation on Resistance of Cotton to Micro-organisms
J. Cyrot *Text. Research J.*, **28**, 1048 (Dec. 1958)

Mercerising cotton with 10–18% caustic soda soln. at room temperature without tension, followed by thorough washing, gives a material which shows a two- to three-fold improvement over the unmercerised material in soil burial tests. In comparative tests, during the time it took a good rotproofed fabric to be degraded, the mercerised sample was degraded and changed 6–8 times and the unmercerised sample 20–30 times.
S.B.D.

Mechanical Properties of Cotton treated with Ethylamine or with Mercerising Caustic
H. M. Ziifle, F. V. Eggerton, and L. Segal
Text. Research J., **29**, 13–20 (Jan. 1959)

Samples of cotton yarn, tyre cord, and fabric were subjected to treatment with anhydrous ethylamine to produce cellulose III. The physical and mechanical properties of these products were compared with those of the untreated materials, containing the cellulose I lattice, and of mercerised cotton, containing the cellulose II lattice. The ethylamine treatment produced effects upon the textile properties of the original materials which were similar to those of slack mercerisation but smaller percentagewise. The properties of the treated cottons apparently were more affected by the accompanying fibre swelling and yarn shrinking than by the shift in the crystal lattice.
S.B.D.

Model Viscose Rayon Filaments
R. J. E. Cumberbirch, D. G. Drummond, J. E. Ford, and S. C. Simmens
J. Textile Inst., **50**, T 262–T 283 (March 1959)

Model viscose rayon filaments have been spun with high deniers (66–75) into coagulating baths with and without zinc salts. As expected, if spun into baths containing zinc a skin is formed on the filament which is absent if the bath is free from zinc. The nature of the skin has been examined by electron and light microscopy, its birefringence has been observed, and staining has been attempted. Because of the higher denier, light microscopy, for example, is facilitated, and the conclusions drawn from the structure of the model fibres are used to make suggestions about the structure of commercial filaments of usual denier.
P.T.S.

Desulphuration of Viscose Rayon Staple Fibre with Surface-active Agents
E. M. Mogilevskii, O. G. Khor'kova, and G. G. Finger
Tekstil. prom., **18**, 9–12 (Nov. 1958)

Structural Crimping of Viscose Rayon Staple Fibres
P. Weber *Textil Praxis*, **14**, 62–68 (Jan. 1959)

The structural crimping of viscose rayon is the result of the torsional differential which is set up between the core and the skin of the filament during the coagulation stage. The number of convolutions per unit length is constant for a given method of yarn preparation but it depends on the denier and the degree of stretch to which the filaments are subjected.
L.A.T.

High-strength Regenerated Cellulose Fibres
D. K. Smith *Text. Research J.*, **29**, 32–40 (Jan. 1959)

Substantial improvements in the physical strength properties of certain fibrous regenerated cellulose products, notably rayon tyre cord, have been achieved during the past decade. These advances in tensile and fatigue properties of tyre cord rayon are reviewed and the factors responsible for the improvements are discussed in such a manner as to point the way for similar quality gains in related products, such as staple fibre. Improvement in properties is primarily attributed to the combined use of physical and chemical actions to accomplish controlled crystallite development and orientation in the spinning filament. Beneficial use has been made of various types of chemical regeneration retarding agents to prolong the plastic-gel state, thereby facilitating heavy stretching along with dehydration of the coagulated filament to yield a highly consolidated and uniaxially orientated structure prior to complete regeneration. The relation of current spinning practices to mechanical properties attained in the final filament are outlined and interpreted in the light of filament cross-sectional structure, secondary swelling properties, and differential dyeing characteristics. Potential strength aims for future cellulosics are discussed and some suggestions made as to the type of products for which the structural skeleton of the cellulose polymer appears to offer outstanding advantages, particularly when coupled with bonding or stabilising resins in intimate molecular association. S.B.D.

Effect of the Chemical Composition of Reagents on the Bonding Strength of Viscose Rayon Cord to Rubber
T. V. Ionova, R. V. Uzina, N. A. Bogomolova, E. M. Mogilevskii, and Z. A. Rogovin
Tekstil. prom., **18**, 35–37 (Aug. 1958)

The effect of the chemical composition of certain agents (e.g. Avirol, Nevoll), used in the treatment of cord, on the strength of binding *S* of viscose rayon cord to rubber is investigated. The introduction of a carboxyl group into the agent decreases *S*, that of an amino group has the opposite effect; in the latter case *S* increases in proportion to the number of methylene groups in the molecule of a diamine (e.g. hexamethylenediamine). Treatment of the cord with dilute soln. of di- and particularly tri-hydroxybenzenes causes a very marked increase in *S*. G.J.K.

Transmission of Ultraviolet Radiation by Silk and Rayon Fabrics in Health Hygiene
P. I. Novoderezhkin
Tekstil. prom., **18**, 51–53 (Sept. 1958)

A comparison of the transmission of ultraviolet radiation (320–450 mμ.) by silk and viscose rayon fabrics of various types is given. Transmission decreases with increasing cloth density and increasing cloth lustre, crêpe georgette fabrics exhibiting highest transmission. The use of lustrous yarn in a matt fabric (e.g. georgette) is recommended on hygienic grounds. G.J.K.

Pore Size of Keratin
D. Harrison and J. B. Speakman
Text. Research J., **28**, 1005–1007 (Dec. 1958)

The extent to which wool may be iodinated with alcoholic soln. of I_2 has been examined as a function of the size of the alcohol molecule. With I_2 in methanol or ethanol, the limiting amount of combined iodine is approximately what would be expected if the whole of the tyrosine were converted to 3,5-di-iodotyrosine. When, however, I_2 in n-propanol is used, the reaction proceeds more slowly and stops before the amount of combined iodine is half the theoretical value. This result and the fact that I_2 in n-butanol and n-pentanol give so small an extent of iodination as to suggest that reaction is confined to the surface of the fibres, confirm an earlier deduction from the elastic properties of wool fibres in alcohols of increasing molecular weight that the fine structure of wool is inaccessible to molecules larger than those of n-propanol. S.B.D.

Strain and the Electrical Resistance of Keratin
J. E. Algie *Text. Research J.*, **29**, 1–6 (Jan. 1959)

The change of resistance with time after the application of various strains to keratin fibres has been examined under standard conditions. There is an initial instantaneous rise of resistance much greater than that due to a dimensional change, which is related to the strain, followed by a decrease in the resistance caused by the uptake of water vapour. A further stage was observed during which the resistance rose as the excess water vapour left the fibre. S.B.D.

Birefringence and Draw Ratio of Man-made Fibres
H. de Vries *J. Polymer Sci.*, **34**, 761–778 (Jan. 1959)

The equation—

$$\frac{d\Delta n}{d\ln\lambda} = m + p\Delta n$$

(Δn = specific birefringence of the fibre; $\ln\lambda$ = natural logarithm of the permanent extension ratio; and m and p are constants) holds for 6,6-nylon, polyethylene, polyethylene terephthalate, and viscose rayon. P.T.S.

Polyhexamethylene - adipamide (6, 6 - Nylon) — Formation of Negatively Birefringent Spherulites
F. Khoury *J. Polymer Sci.*, **33**, 389–403 (Dec. 1958)

When nylon which has originally crystallised in positively birefringent spherulites is heated to a constant temperature within the range ~ 250–265°c. it melts and subsequently crystallises in the form of negatively birefringent spherulites. The number of spherulites formed and their birefringence decrease with increase in temperature within the range above; at 265–266°c. non-birefringent spherulites are formed; above 266°c. no crystallisation was detected. Nucleation is from small polymer aggregates or crystallites, and not from particles of impurity. The crystallinity of the spherulites varies inversely with the temperature at which they are formed. 13 photographs. P.T.S.

Sorption of Hydrochloric Acid by Textile Fibres. IV— Effect on Nylon
P. Larose *Text. Research J.*, **28**, 980–988 (Dec. 1958)

The contraction of nylon yarn resulting from the sorption of HCl has been studied under various conditions. Tension applied to the yarn during the sorption of the gas reduces the contraction in a way that can be explained by the theory of reaction rates. Tensioning of the yarn does not affect the uptake of HCl. The contraction appears to be dependent on the rate of diffusion of the HCl. It also increases with increasing draw ratio, although this effect is strongly influenced by the previous history of the yarn. Twisted nylon filament has also been observed to untwist during HCl sorption. This untwisting also appears to be a rate reaction. S.B.D.

Nitrosation of 6,6-Nylon
M. R. Porter *J. Polymer Sci.*, **33**, 447–455 (Dec. 1958)

The nitrosation was carried out using aqueous and anhydrous nitrous acid, dinitrogen trioxide, or dinitrogen tetroxides. The hydrogen atom of the amide groups of nylon is replaced by a nitroso (NO) group. The same product is obtained from all the nitrosating agents. Yellowing and disintegration begin at 80% nitrosation. The fully substituted nitrosated nylon is a yellow powder. Nitrosated nylon is insoluble in the usual nylon solvents, but soluble in benzene and toluene to some extent. It decomposes explosively at 100–120°c. Below 100°c., heat converts nitrosated nylon almost quantitatively to the polyester by a rearrangement reaction and evolution of nitrogen. The infrared spectrum of nitrosated nylon and heated nitrosated nylon were examined. Some work was also carried out on the chemical properties of nitrosated nylon and the physical properties of the polyester fibre made by heating nitrosated nylon. Free radicals are produced when nitrosated nylon is exposed to light. P.T.S.

Molecular Motions in Polyamides
W. P. Slichter *J. Polymer Sci.*, **35**, 77–92 (Feb. 1959)

Aliphatic polyamides with even numbers of methylene groups between the amide groups melt at higher temperatures than those with odd numbers of methylene groups. X-Ray diffraction of a series of nylons with odd and even numbers of methylene groups over a wide range of temperatures makes it possible to offer some explanation of the phenomenon in terms of crystal structure and changes in structure with changes in temperature. Proton magnetic resonance evidence is consistent. The mechanism of melting is discussed. P.T.S.

ε - Caprolactam— Non - hydrolytic Polymerisation initiated by Hydrogen Chloride
G. M. van der Want and C. A. Kruissink
J. Polymer Sci., **35**, 119–138 (Feb. 1959)

ε-Caprolactam Polymerisation— Mechanism and Kinetics in the Presence of Water. XII— Preparation and Analysis of Poly-ε-caprolactam in the Laboratory
F. Wiloth *Makromol. Chem.*, **27**, 37–50 (June 1958)

The paper discusses the methods of preparing polycaprolactam in the absence and presence of water, methods of carboxyl and amine end-group estimation, and the determination of the intrinsic viscosity of the polymer. P.T.S.

Reactivities of Functional Groups during Polymerisation of ε-Caprolactam
D. Heikens and P. H. Hermans *Makromol. Chem.*, **28**, 246–249 (Dec. 1958)

H. Yumoto and N. Ogata (*Makromol. Chem.*, **25**, 91 (1957)) suggested that the assumption of equal reactivity of end-groups whatever the polymer chain length could not be applied to 6-nylon polymerisation. The authors show that Yumoto and Ogata's results only apply at very low degrees of polymerisation and very high water contents, and that there is no discrepancy between the results of both pairs of workers at higher degrees of polymerisation. *In English.* P.T.S.

Polyamides from ε-Aminocaproic Acid— Equal Reactivity of Amide Groups in Acid Hydrolysis. A Correction.
D. Heikens *J. Polymer Sci.*, **35**, 277–280 (Feb. 1959)

A previous estimation of carboxyl and amine end-groups (see J.S.D.C., **73**, 71 (1957)) involving methanol was shown to be in error. The new results, using an improved technique, confirm that the reactivity of amide groups towards hydrolysis is independent of chain length from the shortest chain (linear dimer) upwards. P.T.S.

Arnel-Dacron (Cellulose Triacetate-Polyester) Wash-and-wear Fabrics
H. F. Elsom and W. T. Westarp *Modern Textiles*, **39**, 40–44 (Oct. 1958)

A brief review of the properties and processing of Arnel–Dacron blends. A.J.

Oligoesters of Terephthalic Acid and Glycol
H. Zahn and B. Seidel *Makromol. Chem.*, **29**, 70–92 (Jan. 1959)

Small polyethylene terephthalate polymers have been prepared with up to 5 units and foreign end-groups. Infrared and X-ray examination show already many similarities with high-mol.wt. polyethylene terephthalate. Crystalline oligomers cannot be dyed with disperse dyes. P.T.S.

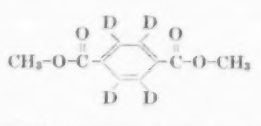
Polyethylene Terephthalate— Strain - induced Crystallisation
A. B. Thompson *J. Polymer Sci.*, **34**, 741–760 (Jan. 1959)

Polyethylene Terephthalate Fibre— Birefringence Transition
S. Sakajiri *J. Polymer Sci.*, **35**, 543–546 (March 1959)

For a polymer of such high intrinsic birefringence as polyethylene terephthalate, birefringence may be an extremely sensitive means of evaluating low degrees of orientation, as in an undrawn filament. Undrawn fibres were prepared with various degrees of orientation and examined at various temperatures by birefringence. Second order transition temperature for fibres of low degree of polymerisation is 65°C., for high degrees of polymerisation, 85°C. P.T.S.

Polyethylene Terephthalate— Infrared Spectroscopy
W. W. Daniels and R. E. Kitson *J. Polymer Sci.*, **33**, 161–170 (Dec. 1958)

The infrared absorption spectra of films of Dacron and Mylar polyesters were investigated, and the deuterated polymer from a small-scale polymerisation of $HO(CD_2)_2OH$ with—



was also examined. Assignments were made for most of the bands in the 2–15 μ. region. Rotational isomerism is put forward as an explanation of the intensity variation of certain bands as the crystalline/amorphous ratio is varied. These bands are present in the spectrum of ethylene dibenzoate, and vary in intensity with change of state. Hydroxyl and carboxyl end-group band intensities can be used to calculate the number-average molecular weight, and the results agree with osmotic pressure determinations. A band assigned to ether linkage absorption indicates some dehydration during the polymerisation. P.T.S.

Nuclear Magnetic Resonance Investigation of Polyethylene Glycol Terephthalate
R. Land, R. E. Richards, and I. M. Ward *Trans. Faraday Soc.*, **55**, 225–231 (Feb. 1959)

Nuclear magnetic resonance spectra of samples of polyethylene glycol terephthalate have been measured over the temperature range 20–465°K. The measured second moments at 20° and 90°K. are greater than the calculated value for a wholly crystalline sample. This is attributed to tangling of molecules in amorphous regions. Low-temperature dynamic loss is restricted to very small molecular motions, but the high-temperature dynamic loss is ascribed to rotation of methylene groups on molecules in amorphous regions. W.R.M.

Polyethylene— Effect of Crystallinity on Viscoelastic Properties
K. Nagamatsu, T. Takemura, T. Yoshitomi, and T. Takemoto *J. Polymer Sci.*, **33**, 515–518 (Dec. 1958)

Acrylonitrile Polymerisation in Aqueous Solution
F. S. Dainton, P. H. Seaman, D. G. L. James, and R. S. Eaton *J. Polymer Sci.*, **34**, 209–228 (Jan. 1959)

The kinetics of the polymerisation of acrylonitrile in aqueous solution by Fenton's reagent or photochemically have been studied over a wide range of conditions. k_p and k_t have been determined by a rotating-sector technique. There is evidence for radical burial in polymer particles. P.T.S.

Acrylonitrile Polymerisation by a Heterogeneous Redox Initiator
Z. Csürös, I. Géczy, B. Zsuffa, and E. Erdös *Makromol. Chem.*, **27**, 171–179 (July 1958)

Acrylonitrile Polymerisation by a Heterogeneous Redox Initiator— Kinetics and Mechanism
Z. Csürös, I. Géczy, and B. Zsuffa *Makromol. Chem.*, **27**, 180–191 (July 1958)

The polymerisation of acrylonitrile in aqueous solution in a hydrogen atmosphere initiated by persulphate ions and a palladium catalyst on barium sulphate. P.T.S.

PATENTS

Regenerated Cellulose of Improved Resistance to Sunlight
Celanese Corpn. of America *USP* 2,862,833

Fibres obtained by the saponification of a stretched wet-spun cellulose ester are given improved resistance to sunlight if an ultraviolet radiation stabiliser is incorporated in them. Resorcinol monobenzoate is a particularly good stabiliser to add to the spinning solution, 0·1–5·0% being effective. Alternatively the fibres may be treated with a solution of resorcinol monobenzoate so as to deposit 0·1–3·0% on them. C.O.C.

Polyacrylonitrile Solutions
Courtaulds *BP* 811,638

A polymer containing ≮ 80% acrylonitrile is readily soluble in a mixture of water, methyl and/or ethyl alcohol, and an alkali metal thiocyanate, alkaline earth metal thiocyanate, ammonium thiocyanate, guanidine, thiocyanate, LiBr, LiI, NaI or $ZnCl_2$. The alcohols form 4–10% by weight of the solvent and the thiocyanate or other salt ≮ 35%. Such a solution is readily de-aerated especially during the stirring necessary during its formation. The solution is used to form fibres by being extruded into water. C.O.C.

Improving the Dyeing Properties of Polyester Fibres
Chemische Fabrik Grünau VEB *BP* 812,111

Treating the fibres at 80–100°C. with the condensates of cyclohexanone or its alkyl nuclear substituted derivatives with a mono- or di-ethanolamine much increases the dyeability of polyester fibres with disperse dyes. This increased dyeability is retained even when the fibres are thoroughly washed or kept for a long time. *N*-cyclohexylidenehydroxyethylamine, *N*-cyclohexylidene dihydroxyethylamine and the corresponding *N*-methylcyclohexylidene compounds are particularly useful in either aqueous or organic solvent solution. C.O.C.

Crimped Synthetic Fibres
ICI *BP* 809,273
Synthetic linear polymer filaments, capable of showing their full crimp after being shrunk, are produced by causing melt-spun filaments, e.g. polyethylene terephthalate, to contact a lubricated solid surface before being wound. W.G.C.

Coating Glass Fibres
J. W. Case *USP* 2,860,450
Coating materials are intimately and strongly bonded to glass fibres if they are applied while the glass is still "nascent", i.e. before they have been exposed to air after the fibres have been formed. C.O.C.

Improved Spinning Properties of Sulphur-dyed Cotton (VIII p. 329)
Metallised Fibres, Yarns, and Fabrics (X p. 335)
Heating of Thermoplastic Synthetic Materials (XIII p. 340)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Mechanism of Detergency
R. P. Harker
J. Textile Inst., **50**, T 189–T 222 (Feb. 1959)
The removal of oily soils from textile fibres— polytetrafluoroethylene, polythene, Terylene, 6,6-nylon, jute, wool, raw wool, and glass— has been followed using a microscope equipped with a cell capable of directing a stream of detergent at the fibre at a chosen temperature. It was observed that the more polar a fibre the more easily oily soil is removed from its surface. If the soil or the fibre is very apolar, then addition of polar substances to the soil will make it more easily removable. 86 photomicrographs of oils being removed from fibres. A theoretical basis for the observed mechanisms of scouring is suggested in many cases. P.T.S.

Detergents, Textiles, and Colour
Textile Institute
J. Textile Inst., **50**, P 161–P 167 (March 1959)
Report of a conference held in Manchester on 11th February 1959. The deterioration of textiles after washing in detergents was discussed from the points of view of a textile manufacturer (C. F. Ward), a detergent manufacturer (F. P. Thompson), and a dye manufacturer (G. S. J. White). The open discussion of the subjects is also reported. P.T.S.

Suspending Action by Detergents in the Presence of Substrate
J. C. Harris *Text. Research J.*, **29**, 99–118 (Feb. 1959)
Soil-suspension tests in the presence of substrate are superior to those made in its absence, but at the expense of increased complexity of the system. Among the factors affecting the soil–substrate relationship are mechanical, chemical, and electrical forces; adsorption of surfactant; deflocculation; sedimentation; soil particle size; and solvation. Surfactants are enhanced in their prevention of soil redeposition by additions of such materials as polyphosphates or silicates, particularly when the calcium ion is suppressed. Non-ionic surfactants are found to be the most effective for preventing redeposition of carbon soils. Considering the complexity of dynamic detergent systems, it is not surprising that a clear mechanism has not yet been advanced to explain soil suspension during the cleaning operation. S.B.D.

Importance of pH in the Processing of Cellulosic Fibres
H. Rath *S.V.F. Fachorgan*, **14**, 21–29 (Jan. 1959)
Owing to the presence of –COOH groups whose degree of dissociation is pH-dependent, cellulosic fibres assume a negative potential when immersed in water. Processes such as wetting, scouring, desizing, bleaching, and dyeing (particularly with azoic combinations) call for pH control to ensure satisfactory results and least fibre damage. L.A.T.

Treatment of Jute with Non-ionic Detergents for Spinning
M. A. Muratova, Z. K. Yakubenko, and B. I. Valov
Tekstil. prom., **18**, 26–30 (Oct. 1958)

Wool Scouring with Non-ionic Detergents
E. M. Bessudova, V. V. Rozhkova, and V. M. Sherishev
Tekstil. prom., **18**, 17–18 (Oct. 1958)

Soiling as one of the Factors influencing Serviceability of Carpets
Z. Sudnik *J. Textile Inst.*, **50**, P 36–P 50 (Jan. 1959)
In testing soil resistance, specimens were tumbled with steel balls and a standard, artificial soil (activated charcoal, finely ground), and after scouring, the degree of soiling was estimated reflectometrically. It was found that oil in the carpet pile, either as a result of inefficient scouring or wicking of oil from the jute backing, was a more important cause of soiling than fibre type or carpet structure. Using fibres with a smooth surface and circular cross-section, or filling in fibre crevices with a dispersion of silica, reduced the tendency to soil. Certain finishing agents also reduced the tendency to soil by filling in the fibre crevices. Tests with artificial soiling methods were compared with results from pieces of carpet in use. P.T.S.

Deposition of Soiling Matter from some Detergent Systems. III— Non-aqueous Systems (continued)
R. E. Wagg *J. Textile Inst.*, **49**, T 561–T 565 (Nov. 1958)
Woollen cloth was agitated in white spirit or trichloroethylene, and the effectiveness of certain additives in preventing the re-deposition of soil was examined reflectometrically. Long-chain fatty acid salts, certain surface-active agents, some oil and petroleum additives, and an aromatic amine inhibit soil re-deposition. Under the experimental conditions used, fatty acids have little effect. Aliphatic amines, and some other surface-active agents sometimes encourage soil re-deposition. The effect of triethanolamine as an additive in white spirit, and of Elektrion R oil in white spirit and in trichloroethylene was examined in detail. The regain of the wool was shown to be involved in some cases. P.T.S.

Bleaching of Linen with Chlorite
O. E. Itina, N. A. Oskorbina, and V. G. Grishina
Tekstil. prom., **18**, 41–43 (Oct. 1958)
A comparative study of bleaching linen with chlorite (I) and hypochlorite (II), respectively, in conjunction with an alkaline scour and hydrogen peroxide aftertreatment, is carried out. The overall times are 10–11 hr. (I) and 18–20 hr. (II). The findings indicate less degradation for a given whiteness with I. Details of the chlorite bleaching process are given. G.J.K.

PATENTS

Bleaching Vegetable Fibres with Formamidine Sulphinate and Alkaline Peroxide
DuP *USP* 2,860,944
Aqueous alkaline solutions of sodium formamidine sulphinate reduce and solubilise dyes similar to the colorants present in cotton, wood pulp and the like. This is made use of e.g. by wetting out samples of unbleached cotton muslin for 2–3 min. at 70–100°C. in a 0·2% solution of a sodium alkyl sulphate and 0·3% sodium pyrophosphate. It is then rinsed and treated for 1–8 min. at the boil in 3% NaOH containing sodium formamidine sulphinate (to yield 0·2% of the acid $HN{:}C(NH_2)SO_2H$). It is again rinsed and boiled for 5 min. in 0·2% H_2O_2 in presence of sodium silicate. The treated samples are brighter and have better mote removal than samples similarly treated in absence of sodium formamidine sulphinate. C.O.C.

Bleaching of Wood Pulp
National Distillers and Chemical Corpn. *USP* 2,865,701
Bleached pulps having improved stability of brightness and strength are obtained by giving the usual chlorination and alkaline extraction or other preliminary treatment and then bleaching with a hypochlorite. The hypochlorite bleach should be adjusted at a high level to give pH 9·5 ± 1·0 in about one-half to two-thirds of the normal bleaching time. This should leave in the pulp 10–35% of the original chlorine in the bath. The pulp is then diluted to 3–6% consistency, brought to pH 5 with H_2SO_4 or HCl, washed off after 1–30 min. and given a final bleach with 0·1–1·0% Na_2O_2 at 140–160°F. C.O.C.

Bleaching Cyanoethylated Cotton with Hydrogen Peroxide
DuP *USP* 2,860,945
Cyanoethylated cotton is bleached without much reduction in its nitrogen content by treating it with

aqueous hydrogen peroxide in presence of a molecularly dehydrated water-soluble phosphate, e.g. sodium pyro- or tripoly-phosphate. The bleach can be improved by giving the cotton a separate treatment, preferably before the peroxide treatment, with an aqueous solution of a formaldehyde sulphoxylate. C.O.C.

Oxidation-reduction Multi-stage Bleaching of Ground Wood Pulp
Virginia Smelting Co. *USP* 2,862,784

Improved bleaching and/or brightness combined with savings in both materials and working costs are obtained if the pulp is treated with a peroxide, preferably sodium peroxide, the slurry stabilised by bringing it to pH 6·0–7·0 with SO_2 or an acid sulphite and finally treated with zinc or sodium hydrosulphite. C.O.C.

Cleansing Raw Wool by Anaerobic Fermentation
A. M. Buswell *USP* 2,864,746

Wool grease and wax can, without any preliminary treatment be converted by anaerobic fermentation into methane and CO_2 without injuring the wool. Thus raw wool (50 parts by weight) was placed in a vessel containing overflow liquor (1750 by vol.) from a sewage disposal plant and containing active methane-producing organisms. The vessel was closed except for an orifice for collecting the gas evolved. The wool and the liquor were kept at 37°c. while being gently agitated. Treatment continued until 68% of the wool grease was destroyed by which time the gas evolved was 142 parts by volume. The wool was then taken out, rinsed, and dried. The treated wool was undamaged and contained none of the vegetable matter present in it before it was processed. C.O.C.

Bleaching Polyacrylonitrile with Chlorite and Oxalic Acid
American Cyanamid Co. *USP* 2,861,864

Gelled (undried) polymers containing $\leq$ 80% of acrylonitrile are readily bleached by alternative treatments with 0·07% aqueous sodium chlorite and 0·02% aqueous oxalic acid respectively at 40–80°c. C.O.C.

Continuous Scouring and Bleaching of Silk and Rayon Fabrics (I p. 315)

VIII— DYEING

Current Books on Dyeing and Textile Chemistry
S.V.F. Fachorgan, **14**, 45–47 (Jan. 1959)

Dyeing Theory
S. M. Neale *Text. Research J.*, **28**, 1041–1044 (Dec. 1958)

The physicochemical approach to the understanding and elucidating of a phenomenon proceeds in three stages – collection of reasonably accurate quantitative data, a qualitative explanation of the observed trends, and finally precise treatment in mathematical terms. The development of dyeing theory passed fairly rapidly through the first two stages during the 1930s and is now entering the third stage. S.B.D.

Dyeing of Cellulose
J. Boulton *Text. Research J.*, **28**, 1022–1030 (Dec. 1958)

The general theory of the dyeing of cellulosic fibres with direct dyes is reviewed, and the influence of such variables as temperature, salt concentration, liquor ratio, and agitation in practical dyeings with direct dyestuffs is discussed. The use of techniques in which vat dyestuffs are applied to the goods in pigment form and then treated to give dyeings of excellent levelness is outlined. The increasing use of blends of cellulosic fibres with non-cellulosic natural and synthetic fibres adds to the complexity of the dyeing operation. One way in which this may be overcome is by colouring the material with resin-bonded pigments. S.B.D.

Improved Spinning Properties of Sulphur-dyed Cotton
N. A. Shubina and G. E. Sladkopevtseva
Tekstil. prom., **18**, 56–58 (Aug. 1958)

For the mélange production of cotton dyed with sulphur dyes in continuous and circulating machines the spinning properties of the fibre are investigated. Improvement is achieved by control of the sodium sulphide concn. (20–30 g./litre for heavy dyeings, and 2–5 g./litre for pale colours), absence of salt in the dyebath, use of a higher bath temp. (85–95°c.), controlled extraction and washing, followed by conditioning and waxing. G.J.K.

Alkaline Pretreatment of Viscose Rayon to improve Dye Affinity
S. A. Vvedenskii *Tekstil. prom.*, **18**, 71 (Aug. 1958)

Viscose staple fabric is given a short (5–10 sec.) treatment in 7–8% caustic soda soln. at 60–70°c., mangled, and washed free from alkali. Improved dye affinity (especially for sulphur and direct dyes) is claimed. G.J.K.

Laboratory Study of Package Dyeing
P. Woerner, F. Fordemwalt, and E. Allen
Text. Research J., **28**, 1031–1041 (Dec. 1958)

In package dyeing with vat dyes by the pigment method, the finely dispersed pigment is circulated through the package and exhausts on the fibre in the oxidised form. The degree of pigmentation varies greatly from one part of the package to another, resulting in initial unlevelness of the package. The degree of levelness of the final dyeing will depend on the amount of migration that takes place after the pigment is reduced to the leuco vat dye. Dyes having leucos with high affinity for the fibre, as is shown by measurements of the free energy of dyeing, migrate less and produce less level package dyeings. Reducing the particle size of the pigment sometimes gives more level pigmentation at the beginning, but this is not necessarily reflected in more level final dyeings. The vat acid process also leads to more uniform pigmentation, but still does not give level dyeings in every case. Retarding agents promote levelness by tying up leuco and slowing down the strike, but are uneconomical, as much dye is left in the bath. Solvents slow the rate of dyeing and promote levelness, but also interfere with exhaustion. Higher temperatures (100–105°c.) promote levelness by reducing exhaustion, which can then be increased by lowering the temperature. However, pressure machines are required and many dyes are unstable at the higher temperatures. A migration test for vat dyes, whereby a dyed and undyed skein are placed in a caustic–hydrosulphite soln. and allowed to reach equilibrium, has been found to give a good indication of the levelling ability of the dye. S.B.D.

Effect of Soaping on Vat Dyeings
L. M. Golomb and M. G. Romanova
Tekstil. prom., **18**, 30–33 (Nov. 1958)

Nine thioindigo dyes are used on Cellophane film and the reflectance measurements, determined before and after soaping (60, 80, and 100°c.) are compared (400–700 mμ.). In most cases soaping brightens colour (shift towards shorter wavelengths), in others colour is deepened (shift towards longer wavelengths). These effects are less marked in the case of dyed fabric. The results show that soaping at temp. above 60°c. in all cases, and above 80°c. in some cases, is essential, whilst length of soaping is not important. Thus, a continuous soaping process is recommended. G.J.K.

Dyeing of Cellulose Acetate with Disperse Dyes
F. Fortess and V. S. Salvin
Text. Research J., **28**, 1009–1021 (Dec. 1958)

The chemical and physical properties of some typical disperse dyes are given, together with their behaviour in the aqueous dyebath and fibre phases. It is observed that the degree of acetylation of the cellulose acetate has a strong influence on the affinity and dyeing rate of the disperse dyes. The relationship of specific dye structure to dyeability and fastness on secondary and triacetates, and the mechanism of carrier dyeing as applied to cellulose triacetate are discussed. The data presented do not fully support either the site dyeing or the solution dyeing hypothesis, but sufficient empirical observations are presented which will increase the control and economy of dyeing with disperse dyes. S.B.D.

Dyes for the Mass Coloration of Cellulose
D. Ts. Kanter, T. A. Nekrasova, and O. M. Golosenko
Tekstil. prom., **18**, 16–17 (Sept. 1958)

Fast dyeings have been obtained using 1:2 metal-complex monoazo dyes (orange, red, and blue–black). G.J.K.

Dyeing Cellulose Acetate from Non-aqueous Media
C. Heit, M. Moncrieff-Yeates, A. Palm, M. Stevens, and H. J. White *Text. Research J.*, **29**, 6–12 (Jan. 1959)

Results are given for the absorption of three disperse dyes by secondary cellulose acetate from solutions in benzene at 25° and 35°c. Additional results are given on the absorption of one of the dyes from solutions in methanol, butyl acetate, and carbon tetrachloride at

25°c. Formally the isotherms can be represented by Langmuir's equation. The results obtained using different solvents show that, in general, the solvents do not act as inert transfer media but effect the basic absorption process for the dye. It is shown that the results can be explained if it is assumed that some solvents compete with the dye for absorption sites within the fibre.
S.B.D.

Dyeing of Wool and Wool Unions with Sulphur Dyes in the Presence of Triethanolamine

N. G. Klemin and P. V. Morÿganov
Tekstil. prom., **18**, 44–47 (Sept. 1958)
C. Weimann *Teintex*, **24**, 113–119 (Feb. 1959)

Wool and wool unions (with viscose and cuprammonium rayons) can be dyed effectively in rope form with sulphur dyes in the presence of triethanolamine using Rongalite and sodium bisulphite (pH 9–10·2) at 65–70°c. for 20–30 min., followed by careful rinsing at the conclusion of dyeing. In all cases fast dyeings can be obtained, and the following figures are quoted: weathering 5–4, light 4–5, dry rubbing 3–3·5, wet rubbing 2·5, laundry washing 5/5, water 5/5, perspiration 5/5–4. Union materials are dyed to a solid colour. The leuco compound is stable to air oxidation during winch dyeing. The application of this technique in continuous dyeing methods is recommended.
G.J.K.

Effect of pH on the Uptake of Anionic Dyes by Polyamide Fibres

E. Elöd, K. Schupp, and V. Nakahara
S.V.F. Fachorgan, **14**, 30–34 (Jan. 1959)

Diffusion coefficients and saturation values of acid dyes and 1:2 metal complexes exhibit well defined maxima when the pH of the dyebath is varied. The former dye anions combine with the positively charged sites in the fibre, and the 1:2 metal complexes are taken up by the fibre because they are more soluble in the substrate than in the water. The degree of aggregation of the latter complexes in soln. is sensitive to the addition of acids and electrolytes.
L.A.T.

PATENTS

Tone in Tone Effects by Dyeing Wool Material

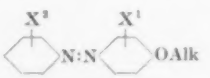
H. Harrison & Co. (Finishers) *BP* 811,702

The material is subjected to ultraviolet radiation in patterns before it is dyed. Thus knitted wool fabric was exposed through a metal stencil for 4 min. to the radiation from a high pressure mercury vapour lamp 6 in. away. On being dyed with Wool Blue RL (C.I. Acid Blue 92) from a bath containing ammonium and sodium sulphates the irradiated portions of the material were dyed dark blue and the unexposed portions light blue.
C.O.C.

Fast to Light Yellow to Orange Dyeings on Polyesters with Disperse Dyes

FH *BP* 811,723

Yellow to orange dyeings of very good fastness to light are obtained on polyesters by use of disperse dyes of formula—

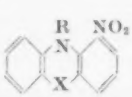


(X^1 and X^2 are optional substituents; X^1 being Hal, Alk or alkoxy, and X^2 Hal, Alk, alkoxy or nitro). Thus 4-methoxy-1,1′-azobenzene yields bright yellow dyeings and 2,4-dimethoxy-4′-nitro-1,1′-azobenzene yields orange dyeings.
C.O.C.

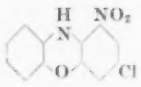
Disperse Dyeing of Polyesters

BASF *BP* 812,109

Dyes of formula—



(X = O, S or CO; R = H, Alk, Ar or aralkyl; either or both of the benzene rings can be substituted by neutral atoms or radicals) when applied to polyesters from aqueous dispersion or organic solvent solution give pale yellow to bluish-red dyeings of good to very good fastness properties. Thus Terylene fabric pressure dyed for 60 min. at 130°c. with the dye

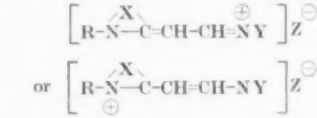


using as carrier the Na salt of a bis-(alkylsulphone)-imide obtained according to *BP* 676,857 (J.S.D.C., **68**, 401 (1952)) becomes bordeaux of very good fastness to water and rubbing and good fastness to light.
C.O.C.

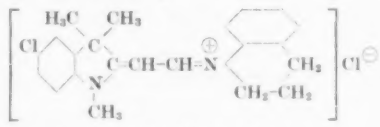
Dyeing Polyacrylonitrile Fibres with Basic Dyes

BASF *BP* 809,382

Fast yellow to orange dyeings on linear polyacrylonitriles, or copolymers containing acrylonitrile, from acid, neutral or weakly alkaline baths, are produced using the basic dyes



(R = Alk, cycloAlk, Ar, aralkyl; X and Y = divalent groups forming 5–6 membered heterocyclic rings with the N atoms; Z = anion of an acid of dissociation constant 10^{-1} to 10^{-6}). Thus, a level yellow dyeing of excellent fastness is obtained using



from a dilute acetic acid bath at the boil.
E.T.

Basic Vinyl Polymers for Improving the Fastness of Direct Dyes (III p. 317)
Non-crystallising Phthalocyanine Pigments (IV p. 319)
Improving the Dyeing Properties of Polyester Fibres (VI p. 327)
Fixing Pigments on Fibrous Materials or Foils (IX p. 331)
Effect of Crease-proofing Agents on the Light Fastness of Sensitive Dyes (X p. 333)

IX—PRINTING

Three-colour Printing on Fabrics

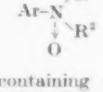
A. A. Sinegub-Lavrenko
Tekstil. prom., **18**, 50–51 (Aug. 1958)

PATENTS

Tertiary Amine Oxides—Vat Printing Auxiliaries

ICI *BP* 811,046

Brighter and stronger prints are obtained from vat dye *leuco*-sulphuric ester printing pastes to which are added N-oxides of tertiary amines—



(Ar = benzene ring containing ≥ 1 SO_3H or COOH; R^1, R^2 = Alk or subst. Alk). The compounds are made by reacting an amine $Ar{-}NR^1R^2$ with H_2O_2, or a compound giving H_2O_2 on treatment with water, e.g. perbenzoic acid, permonosulphuric acid. Reaction occurs in water or aq. acetone at 70–80°c., excess H_2O_2 is decomposed by Pt black and the products are isolated from the filtered solutions by vacuum evaporation.
E.T.

Pigment Printing using Aqueous Aminoplast Emulsions

American Cyanamid Co. *USP* 2,863,788

A water-in-oil emulsion of a urea or triazine aminoplast and a pigment is used, there being present in the aqueous phase a low-mol.wt. alcohol. The pH of the emulsion must be > 9. Such an emulsion is very suitable for use with photogravure cylinders or extremely fine mill and die engravings as they do not spread on the cloth after printing and so yield clear cut prints. The prints obtained have good resistance to dry cleaning. Any type of pigment may be used but the process is particularly suitable for

leafing metallic pigments. Thus a "print base" is made up of Aluminium Flake (C.I. Pigment Metal 1) (15), methanol (15) and 80% melamine resin precondensate (70). A "reduction concentrate" is made up of a 30–40% styrene–20–30% phthalic anhydride copolymer (64) in xylene (8) to which is added $(NH_4)_2SO_4$ (8) in water (20). The copolymer must have a Gardner–Holdt viscosity of W to Z, at 50% solids in a mixture of equivalent of mineral spirits and xylene. A printing paste is then made up of print base (200), water (172·5), reduction concentrate (12·5), xylene (17·5) and mineral spirits (97·5). This paste contains 6% pigment and has pH 7·7. When printed on to a fabric and baked it imparts improved reflecting properties that remain unaffected by five dry cleanings. C.O.C.

Printing Wool with Insoluble Reactive Dyes
ICI *BP* 809,204

Wool is printed, especially mélange-printed, by applying a water-insoluble colourant, or intermediate, containing a mono- or di-halogeno-1,3,5-triazin-2-ylamino group, and then steaming. These products are made by reacting a cyanuric halide with dyes of the nitro, azo or anthraquinone series containing a primary or secondary amino group, or with the diazo component or the coupling component of suitable azoic combinations. Thus the monoazo compound obtained by coupling diazotised 4-amino-3-chlorophenyl ethyl sulphone with the condensation product of 1 mol. of 2,4-dichloro-6-methoxy-1,3,5-triazine and 1 mol. of *N*-β-hydroxyethyl-*N*-β′-aminoethylaniline is applied to wool as a suitably thickened printing paste, and steamed after drying, to give an orange. E.S.

Fixing Pigments on Fibrous Materials or Foils
FH *BP* 810,548

An aqueous bath or paste containing pigment, an alkali-soluble resinous condensate containing carboxylic acid groups (obtained by treating a polycarboxylic acid with a polyhydric alcohol), and a polyfunctional compound whose functional groups containing a three-membered ring containing N or O is used. The impregnated or printed material is then heated, if desired, in presence of steam. The dyed or printed material is especially resistant to mechanical treatment in washing liquors. C.O.C.

Mash Block Transfer Printing
Congoleum-Nairn *USP* 2,860,069

A backing material 6–12 ft. wide is passed intermittently in stepwise fashion beneath a number of printing blocks in a flat bed printing machine. These blocks extend across the full width of the backing and are 18 in. wide and 18 in. apart. Associated with each block there is a paint reservoir within which a hard surfaced roller revolves. When this roller moves across the printing surface of the block careful control of the clearance between the roller and block allows a uniform film of paint to be transferred to the block. These printing blocks are only depressed upon the backing after every second advance of it. This cycle is repeated until the complete design is impressed on the backing as a series of 18 in. stripes 18 in. apart. After the desired design is complete the backing moves beneath a series of transfer blocks arranged exactly as the printing blocks but having no paint reservoirs associated with them. These transfer blocks reciprocate with every advance of the backing. When they come down on a previously printed stripe they remove some of the paint from it, which paint on their next downward motion they deposit upon a previously unprinted stripe of the backing. This results in the whole of the surface of the backing being covered with stripes of paint. C.O.C.

Stencil Screens Resistant to Prolonged Heating
DuP *USP* 2,860,576

The design is first formed on the screen as a negative, the meshes of the design being filled with a soluble, light-hardened material. The open meshes of the design are then filled with a polytetrafluoroethylene or polysilicone resin and after this has been fixed by heat the soluble light hardened material is dissolved from the screen. This leaves a positive of the desired design with filled meshes of a heat-resistant, insoluble polytetrafluoroethylene or polysilicone. C.O.C.

Improving the Printability of Polyethylene and Similar Plastic Sheeting
Olin Mathieson Chemical Corpn. *USP* 2,859,480

Treating the surface of the sheeting with an electric glow discharge, advantageously a continuous high frequency and high voltage glow discharge, preferably while hot, much increases the ability of printing inks to adhere to it. C.O.C.

Hectograph Process and Solvent
General Aniline *USP* 2,862,444

Incorporating a little butyrolactone in a hectograph solvent consisting mainly of methanol or ethanol, much reduces the inflammability of the solvent and results in improved copies. Improvement of the copies is particularly outstanding in the case of solvents containing a chlorinated hydrocarbon. C.O.C.

Transfer Sheet or Carbon Paper containing a Metallic Salt and a Hydrotrope
Ditto *USP* 2,864,720

Addition of a hydrotrope, e.g. sodium cymene sulphonate and butyl naphthalene sulphonates, to transfer sheets of the type in which a base sheet is coated with an oleaginous and waxy material and a metal salt and which is used in conjunction with copy sheets containing a substance with a reagent which reacts with the metal to form a water-insoluble dye, e.g. rubeanic acid or glyoxime, results in copies of stronger intensity. C.O.C.

Duplicating Process using Fluorescence in Photographic Emulsions
General Aniline *USP* 2,865,744

Irradiation with blue light of photographic emulsion containing sensitising dyes causes a fluorescence in the region of wavelengths longer than blue. This fluorescence can be recorded by panchromatic materials after all of the blue light passing through the fluorescing emulsion has been eliminated by a yellow filter. This can be made use of to obtain direct copies from a transparent negative or positive by placing it over a transparent support bearing a silver halide emulsion sensitised with 1,1′-diethyl-2,2′-cyanine iodide and then exposing it for a time longer than that required to form a latent image and long enough to destroy in the heavily exposed areas the ability to fluoresce without affecting that ability in the areas of low exposure. The original is removed and panchromatic printing material exposed to blue light through the intermediate printing already obtained, there being a yellow filter between these two which absorbs all the blue light but transmits the fluorescent light emitted by the intermediate printing. The panchromatic material is then developed to produce a duplicate picture of the original. C.O.C.

Old Ivory and Buff Tints on Photographic Paper
Eastman Kodak Co. *USP* 2,865,746

Photographic prints after being fixed are treated with the sodium salt of sulphonated lignin to produce, dependent on the amount used, light ivory to buff tints on the paper. C.O.C.

Improving Colour Reproduction in Colour Photography
Agfa *BP* 811,311

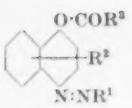
A process for producing colour-corrected colour separation records or colour-corrected multicolour images by the negative-positive process from a multi-colour image. C.O.C.

Colour Photography
Ilford *BP* 811,185

Addition to the colour developing solution of $\geq$ 0·5 g./l. of a 3-pyrazolidone type of developer, particularly 1-phenyl-3-pyrazolidone, reduces the tendency for an image to develop in the unexposed silver halide of adjacent layers. In addition the activity of the developer is much increased and so denser dye images are obtained. Other advantages are that the grain of the final dye image is made more even and smooth in appearance and in some cases the hue of the dye formed is improved. C.O.C.

Colour Couplers and Photographic Colour Correction
Eastman Kodak Co. *USP* 2,860,974

Compounds of formula—



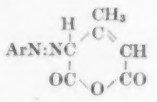
(R^1 = aromatic group which renders the compound non-diffusing, e.g. naphthalene; R^2 = a solubilising group; R^3 = nitrophenyl or cyanophenyl as auxochrome) are non-image-forming colour couplers which transmit green and red light. They couple in the exposed region of an emulsion layer to form a soluble dye which washes out and leaves that portion of the coupler which is in the unexposed region as a coloured masking image. They are initially light coloured, e.g. yellow, but removal of the masking group on the auxochrome readily changes them to a colour, e.g. magenta, which absorbs green light. This enables them to be used in the blue-sensitive layer of a multilayer coupler film without the couplers interfering with the exposure to red or green light of the underlying layers. After such exposure they are then changed to the green light absorbing form. C.O.C.

Photographic Colour Correction using 2-Azo-1-Naphthol Dyes
Eastman Kodak Co. *USP* 2,860,975

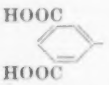
2-Azo-1-naphthol dyes not substituted in the 3- or 4-positions of the naphthol nucleus can be used as coloured couplers in the processes described in *USP* 2,449,966; 2,657,134; 2,428,054; 2,455,169; and 2,521,908. When they react with the oxidised colour developer they yield yellowish to brown products of low tinctorial power which do not adversely affect dye images produced in the same region from colourless couplers. They can then be utilised to provide masking images of a wide variety of colours. C.O.C.

Azo Dyes as Filters in Colour Photography
Eastman Kodak Co. *USP* 2,860,979

Dyes of formula—



e.g. where Ar =



can be used as photographic light screens which are easily removed during normal processing. C.O.C.

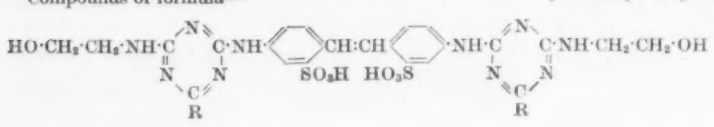
Colour Photography in which Dye Formation is Carried out after Removal of the Silver Halide
Eastman Kodak Co. *USP* 2,865,747

The colour couplers and a hydroquinone derivative, e.g. s-octadecylhydroquinone are dispersed in the silver halide emulsion layer. After exposure the emulsion is developed in a black-and-white developer the oxidised product of which oxidises the hydroquinone derivative to yield a quinonoid image *in situ* with the silver image, e.g. 1-phenyl-3-pyrazolidone. The emulsion is then bleached and fixed to give the silver and the silver halide. Finally it is treated in an alkaline solution of a colour developer to produce the dye image, e.g. with 2-amino-5-diethylamino toluene hydrochloride. With 2-(2′,4′-di-t-amylphenoxyacetamido)-4 6-dichloro-5-methyl phenol as the colour coupler a blue image is obtained and with α-{3-[α-(2,4-di-t-amylphenoxy)acetamido]benzoyl}-2-methoxyacetanilide, a yellow image. C.O.C.

Mixtures of Polymethin Dyes and Pyridine or Ketone Compounds as Photographic Supersensitisers
Eastman Kodak Co. *USP* 2,860,981–4

Fluorescent Brightening Agent for use in Photographic Paper or Emulsions
ICI *BP* 811,182

Compounds of formula—



(R = Cl, phenylamino or diphenylamino) are used, preferably in the emulsion or in the subbing layer or supercoat. They are unaffected by exposure to ultraviolet radiation and photographic processing and so their use results in the prints having pure whites. C.O.C.

Extending the Spectral Sensitivity of Photoconductive Materials used in Electrostatic Printing and Copying Processes.
Radio Corpn. of America *BP* 811,165

The sensitivity of electrostatic printing materials containing zinc oxide as the photoconductive material is extended beyond the range of 3750–3900 A. by use of an organic dye which absorbs radiant energy and transfers it to the zinc oxide. The following dyes are suitable for this purpose—C.I. Acid Yellow 73; C.I. Acid Red 51, 87, and 94; C.I. Mordant Red 3; C.I. 58050; C.I. Basic Orange 14, C.I. Basic Blue 12, C.I. Basic Green 1 and 4; C.I. 42590; C.I. Basic Violet 3; C.I. Basic Black 1; Kryptocyanine and Pinacyanole. C.O.C.

Continuous Screen Printing (I p. 316)
Colour Developers (IV p. 320)
Cyanide of Soluble Blue (C.I. 42755)—Use in Photocopying Paper (IV p. 323)
Transfer Paper, Typewriter Ribbons, etc. (V p. 325)
Felt Base Floor Covering having a Decorative Wearing Surface (X p. 335)
Variegated Colour Coating of Cloth or Plastic Sheeting (X p. 335)
Electrolytic Recording Paper (XI p. 338)
Heat-sensitive Copying Sheets (XI p. 338)

X—SIZING AND FINISHING

Smoothness of Cotton Fabrics
C. F. Goldthwait, R. D. Kirby, S. Fretwell, and H. Wiehart *Text. Research J.*, **29**, 134–143 (Feb. 1959)

An exploratory research has sought the most promising ways of imparting a high degree of durable smoothness to cotton cloth. This work, limited to laboratory procedures, has resulted in finishes characterised by different degrees of smoothness, of glaze, and of durability. Smoothness was very well retained in the best of these finishes and can be considered permanent, although the glaze gradually decreased on washing. Some of these finishes seem readily adaptable to lining and other apparel fabrics. The work was based on the use of an experimental calender and largely upon the calendering of cloth while it was wet, in a state of swelling greater than that from mere wetting with water. There would be difficulties in practical operation if the water in the cloth contained dissolved finishing agents or if the cloth was too wet. Objections have been partially met by preswelling, washing, padding the wet cloth in a softening and fixing agent, and then drying before calendering. Further lines of approach suggested are partial drying before calendering and the use of higher calender temperatures and pressures. S.B.D.

Mechanical Properties of Chemically Modified Cottons
C. M. Conrad *J. Textile Inst.*, **50**, T 133–T 160 (Jan. 1959)

Chemical modifications were substitution of OH groups in cellulose by acetyl, cyanoethyl, carboxymethyl, carboxyethyl, and benzyl groups. The mechanical properties measured included yarn knot strength, breaking strength, Elmendorf tearing strength, ultimate elongation, average tensile and flexural stiffness, work to rupture, frictional behaviour, creep, elastic recovery, resilience, and abrasion resistance, flat and flex. Density changes were also investigated. The changes in mechanical properties depended whether fibre, yarn or fabric was used for the tests. In general, fibres lose strength after substitution although at very low substitution carboxymethylation improves fibre strength. Similarly, most of the mechanical properties of cotton fabrics, yarns or fibres are not improved by chemical substitution except, in some cases, by carboxymethylation. 27 tables. P.T.S.

Permanent Set in Cotton and the Physical Mechanism of Wrinkle-resistant Treatments
M. DuPré *Text. Research J.*, **29**, 151–155 (Feb. 1959)

Permanent set can be given to a

cotton fibre by the structural elements slipping into new positions of mechanical equilibrium and not returning to their former relative positions when the deforming force is removed. Wrinkle resistant treatments cross link these elements, reduce their relative movement, and increase their elastic recovery, thereby giving a more wrinkle resistant fabric. Data are presented and discussed for three possible modes of slipping—between the structural elements in the microfibrils, between the fibrils, and between the growth layers. S.B.D.

Imparting Crease Resistance and Crease Retention to Cotton with Tris-1-aziridinylphosphine Oxide
G. L. Drake and J. D. Guthrie
Text. Research J., **29**, 155–164 (Feb. 1959)

Cotton fabric can be made crease-resistant by padding it with an aqueous solution of tris-1-aziridinylphosphine oxide containing catalytic quantities of zinc fluoborate, drying at 80–90°c. for 4 min., and curing at 140°c. for 4 min., following with a good wash. Crease recovery depends on the resin add-on and it can be increased by an aftertreatment with octadecylethylene-urea. The crease recovery is not changed much by home laundering. Fabrics having high crease recovery angles are observed to have an appreciable loss in tear strength. The resin cannot be stripped from the fabric by methods that are effective for other resins. In addition to imparting crease resistance, the resin also imparts some degree of flame resistance. S.B.D.

Triazones—Creaseproofing Agents for Cotton
R. L. Wayland *Text. Research J.*, **29**, 170–179 (Feb. 1959)

Although the triazones have been known for a long time as chemical compounds, they have only recently come into prominence as creaseproofing agents. Fabrics treated with pure triazone resins show no damage due to retained chlorine and, when mixed with resins normally exhibiting high damage due to retained chlorine, they exert a chlorine damage depressant effect. Triazone resin finishes compare favourably with the best nitrogenous resin finishes in respect to durability and crease resistance–fabric strength relationships. Fabrics treated with triazone resins show some tendency to discolour at elevated temperatures, but this discoloration can be easily removed. Although the resins have been blamed for imparting odour to fabrics, this has not been a problem in commercial usage where properly prepared resins and proper treating conditions have been employed. The triazone resins have now been used commercially on a large scale and have been found to be a valuable addition to the finisher's line of creaseproofing materials. S.B.D.

Performance Characteristics of a New Triazine–Formaldehyde-based Cross-linking Agent for Cellulosic Fabrics
T. F. Cooke and P. B. Roth
Text. Research J., **29**, 180–190 (Feb. 1959)

Performance characteristics are described and some of the properties of the resin compared with those of two other commercially important finishing agents, ethylene-urea–formaldehyde and triazone–formaldehyde. Applied to cotton fabrics the resin provides a wide range of wet and dry wrinkle recovery values with only moderate decreases in tensile strength. The finish shows good resistance to chlorine, as measured by strength loss and discoloration under practical laundering conditions. It shows low soil pick-up during washing and is resistant to acid hydrolysis. The resin does not present a fish odour and exhibits a minimum of formaldehyde smell. S.B.D.

Formic Acid Colloid of Methylolmelamine as a Weather- and Rot-resistant Finish for Cotton
W. N. Berard, G. A. Gautreaux, and W. A. Reeves
Text. Research J., **29**, 126–133 (Feb. 1959)

A study of application techniques of methylolmelamine resins to cotton has revealed a practical method for producing cotton fabric with outstanding rot resistance and improved weather resistance. The method is based on the use of fresh formic acid colloids of methylolmelamine in a pad–dry–cure process. Cotton fabric finished with the acid colloids compare favourably with acetylated or cyanoethylated fabrics which are known to have excellent resistance to rot. Several acids were evaluated for colloid production but only formic acid produced suitable colloids. A number of metal halides have been used as catalysts with the colloids. Small amounts of metal become tenaciously held by the fabric, and in some cases can alter outdoor weathering and other properties of the fabric. S.B.D.

Amine Odour in Resin-treated Fabrics
A. C. Nuessle, E. O. J. Heiges, and R. A. Olney
Text. Research J., **29**, 41–54 (Jan. 1959)

Epoxy Resin Blended Finishes for White Cotton
D. D. Gagliardi and F. B. Shippee
Text. Research J., **29**, 54–65 (Jan. 1959)

New finishes based on blends of epoxy resins with selected aldehydes, acetals, formaldehyde-amino resins and polymeric materials such as silicones, polyethylene, polyacrylates, and epoxy-based plasticisers have been explored to produce new and improved effects on white cotton. With some of the formulated blends, durable wash and wear finishes, crease resistance, and dimensional stability are obtained which will withstand repeated laundering and chlorine bleaching operations. An outstanding finish for white cottons has been developed based on combinations of epoxy resins with dimethylolethylene urea. The practical conditions of cloth preparation, drying and curing cycles, choice of catalysts, washing procedures, and afterfinishing operations are described for optimum results. Also discussed are the limitations of these and other presently available finishes for cotton, with special emphasis on some of the theoretical possibilities for new cotton fibre modification. S.B.D.

Effect of Crease-proofing Agents on the Light Fastness of Sensitive Dyes
H. B. Goldstein and D. N. Koenig
Text. Research J., **29**, 66–73 (Jan. 1959)

The light fastness of several classes of dyes is known to be greatly affected by certain types of finishing agents such as cationic softeners and conventional types of crease-proofing agents. Data are presented to show the effect of most of the presently available creaseproofing agents on the light fastness of the direct, azoic, and reactive classes of dyes and also a few selected vat dyes. S.B.D.

Cotton Finishing with Acetal Reactants
J. B. Irvine, T. J. Cronin, and J. H. Davids
Text. Research J., **29**, 74–88 (Jan. 1959)

An acetal cellulose reactant which imparts a high crease resistance to fabrics is discussed. Determination of the optimum conditions of application in the laboratory are followed by discussion of several applications in textile mills. A catalyst which permits rapid low-temperature curing of acetal reactants is also discussed, and results of mill usage are given. An efficiency factor relating crease resistance increase to tensile loss is suggested. S.B.D.

Chlorine Retention in Resin-treated Cottons
H. H. Mosher *Text. Research J.*, **29**, 88–95 (Jan. 1959)

A study of cyclic urea–formaldehyde finishes in general and dimethylolurea in particular shows that they may undergo a change during ageing or laundering giving rise to materials which can retain chlorine. This change can be minimised, but not entirely prevented, by using a high concentration of catalyst and elevated curing temperatures. Besides ageing and laundering, storage under acidic conditions and, possibly, sunlight are thought to promote chlorine retention damage. Maintaining the fabric slightly alkaline is usually sufficient to protect it in all excepting the more vigorous laundering, bleaching, and ironing treatments. S.B.D.

Chlorine Retention of Aminoplasts and other Nitrogen-containing Formaldehyde Resins
R. Allscher *Textil Praxis*, **14**, 73–76 (Jan. 1959)

A detailed account is given of the experimental work designed to evaluate chlorine absorption of urea–formaldehyde resins. The molecular ratio of the reactants is 1:1, 1:1·8, and 1:2·5, using 20 ml. of 10% NH_4Cl per litre as catalyst. The samples are dried at 70°c., cured for 4 min. at 130°c., and 5 min. at 150°c. Resins or resin-treated fabrics are subjected to NaOCl soln. (1 g. available Cl per litre), at room temp., for ½, 1, 4, and 8 hr. The consumption of Cl was estimated by iodometric titration. Results are tabulated and presented in the form of histograms. It is evident that chlorine absorption of urea–formaldehyde resins depends on the molecular ratio of the reactants and the solid content of the precondensate. It is markedly influenced by the conditions of curing and

invariably increases with the duration of chlorination. Ethyleneurea–formaldehyde resins do not retain chlorine. L.A.T.

Treatment of Wool Cloth with Concentrated Sulphuric Acid

J. W. Bell and C. S. Whewell

J. Textile Inst., **49**, T 706 (Dec. 1958)

Wool is "wetted" immediately by conc. sulphuric acid. Slight degradation occurs if the treatment is for 20 sec. and is followed by rinsing in large volumes of water. The cloth shrinks 10% in warp and weft directions; it is resistant to dyeing with Solway Blue B if the acid is 100% concentrated, but not if it is 95% or less; treated with 100% acid it is completely shrink-resistant during hand-milling when a control sample shrinks 33·5%. P.T.S.

Permanent Lustring of All-wool Fabrics

J. B. Speakman and M. A. Wolfram

J. Textile Inst., **49**, T 627–T 628 (Nov. 1958)

A high lustre can be imparted to a wool fabric by impregnating the fabric with a solution of sodium bisulphite (a setting agent) in a solvent less volatile than water (e.g. a water–ethylene glycol mixture) and pressing the fabric between an electrically heated base plate with a highly polished surface and a weighted metal ring for a short time. The lustre is fast to washing at 40°c. in a dilute Teepol solution, and fast to steaming in the Hoffman press. P.T.S.

Effect of Silicones on the Properties of Wool

G. Nitschke

Faserforsch. und Textiltech., **9**, 530–536 (Dec. 1958)

The influence of various silicones on some properties of wool are studied. Moisture absorption, alkali and acid solubility, damage, extensibility, swelling, and felting are among the properties studied. W.R.M.

Polyamine Resins for Finishing of Hydrophobic Fibres

E. I. Valko and G. C. Tesoro

Text. Research J., **29**, 21–31 (Jan. 1959)

Finishes designed to protect textiles against accumulation of static must possess hygroscopicity, high ionic concentration, and resistance to washing and dry cleaning. Polyelectrolytes deposited from aqueous solution and cross-linked on the fibre satisfy these conditions. Polyamines cross-linked by alkylation with polyhalides were selected to study the correlation between structure and antistatic performance. The gelling time of polyamine–polyhalide mixtures supplied a good indication of the suitability of the reactants to form durable antistatic finishes on the fibre. Some correlation between the degree of polymerisation and the branching of the polymers and their antistatic performance was established. S.B.D.

PATENTS

False Twist Yarns

Giuseppe Dubini & C. S.A. *BP* 809,002

Simplified apparatus for the production of false twist yarns in which the heat treatment is more readily controlled than in previous systems. W.G.C.

Rendering Cellulosic Materials Resistant to Acid

American Cyanamid Co. *USP* 2,864,723

The fabric is impregnated with at least 10% of its weight of a water-soluble Group II metal salt and dried. It is then treated with a compound which converts the metal into a water-insoluble oxide or hydroxide and again dried. It is also treated with an aminoplast resin either simultaneously with one of the above treatments or after them. Thus cotton cloth was impregnated with $MgCl_2$, dried, treated with ammonia, again dried and then given a melamine resin finish. The treated cloth impregnated with 80% of its weight of 5% HCl, steamed for 5 min. in a Hoffman press and pressed dry had the same tensile strength as an untreated piece tested in the same way. C.O.C.

Cyanoethylation of Cellulose by Treatment with Acrylonitrile

Monsanto *USP* 2,860,946

Cellulose impregnated with an aqueous solution of a strongly alkaline hydroxide is continuously passed into acrylonitrile vapours maintained at 70–80°c. with continuous withdrawal of an acrylonitrile–water azeotrope from the apparatus. The cyanoethylated cotton obtained is washed and dried. This method results in much reduced formation of $\beta\beta'$-oxydipropionitrile as a byproduct during the cyanoethylation. C.O.C.

Cyanoethylation of Cellulose

American Cyanamid Co. *BP* 812,063

The cellulose is treated with acrylonitrile in presence of water, an alkali metal hydroxide and an inorganic water-soluble salt of an alkali metal, until the desired degree of cyanoethylation has been obtained. The presence of the salt speeds up the rate of cyanoethylation. NaI, Na phosphates and NaCNS being especially effective. C.O.C.

Reducing the Tendency of Wool to Felt

Wool Industries Research Assocn. *BP* 810,439

The wool is first treated with a dilute aqueous organic peracid of formula R·CO·O·OH (R = H or Alk) or of persulphuric acid and then with an aqueous solution of a halogen or an acidified hypohalite. Thus wool hosiery fabric (100 parts) is treated with an aqueous solution (3000) containing peracetic acid (3) and an anionic wetting agent (3) at 15°c. for 30 min. It is then rinsed in cold water and treated for 20 min. in water (3000) containing Na hypochlorite (3·1) and 36% hydrochloric acid (8·5). C.O.C.

Water Repellent Finish

Montclair Research Corpn. and Ellis-Foster Co. *USP* 2,861,054

The water-dispersible products obtained by reacting together a higher fatty acid amide, formaldehyde, a carbamido compound and a taurinating agent are used for rendering textiles, etc. water-repellent or as coating agents for textiles. Thus a mixture of melamine, paraformaldehyde, morpholine, stearamide, candelilla wax and *n*-propanol was heated at 80–90°c. for 3 hr. The sodium salt of *N*-methyl taurine was then slowly added and heating continued for 1 hr. The product when dispersed in water containing 5% (on the weight of the product) each of urea and NH_4Cl was used for impregnating cotton cloth. The cloth was then dried at 60°c. and baked at 150–155°c. for 5 min. This yielded an excellent water-repellent finish of good fastness to laundering. C.O.C.

Durable, Stiff, Crisp Finish on Polyamide Textiles

ICI *BP* 811,735

The materials are treated with an aqueous solution of the ammonium salt of an acrylic acid polymer and a polyhydric alcohol, if desired in presence of an acid catalyst, and then dried and baked. The finish obtained is resistant to severe alkaline scouring. Thus 2-oz. nylon twill is impregnated with 76% of its dry weight of a solution containing the ammonium salt of an acrylic acid polymer (4·5) and glycerol (1·5) in water (94) at 20°c. It is finally dried at 50°c. and baked for 30 min. at 150°c. This yields a stiff, crisp finish resistant to washing with soap and soda at 100°c. and to dry cleaning. C.O.C.

Water-repellent Finish using Dextran Esters

Commonwealth Engineering Co. of Ohio *BP* 810,565

Coating textiles with a dextran ester of a fatty acid of 8–18 C imparts both dimensional stability and a water-repellent finish which is resistant to laundering. Thus cotton poplin impregnated with a 5% solution in carbon tetrachloride of dextran palmitate containing 2·9 palmitoyl radicals per anhydroglucopyranosidic unit, dried and laundered four times, has excellent water-repellency. C.O.C.

Poly(ethylene Terephthalate) Yarns and Fabrics having a Dry Crêpe-like Handle

DuP *BP* 812,110

Fabric made from continuous filaments of poly(ethylene terephthalate), which vary in denier along their length show a dry crêpe-like handle after they have been heated to > 90°c. and, when dyed, have a speckled appearance. This speckled appearance is enhanced if the fabric is dyed at < 90°c. before being heated to above that temperature. C.O.C.

Back Filling of Carpets

British Cotton Industry Research Assocn. *BP* 812,013

The filling material is supplied to a tank from which it is applied to the carpet by a finishing roller. The rate at which it is supplied to the tank is calculated from the speed of the carpet and the amount of filling it is desired to give. Any change in the amount of filling material taken from the tank caused by deviation in the actual rate of application of filling from that prescribed is used to alter the

relationship between the carpet and the finishing roller so as to correct the deviation. C.O.C.

Felt Base Floor Covering having a Decorative Wearing Surface

Bonafide Mills *USP* 2,860,071

A felt base is treated first with a seal coating and then with a vinyl print coating. Good adhesion between the two coatings, particularly when the seal coating has an oleoresinous base, is obtained by embodying in the print coating a solution of a vinylchloride–vinylidene chloride copolymer containing $< 20\%$ of vinylidene chloride, e.g. Geon Resin 200×20 (Goodrich Chemical Co.). C.O.C.

Imparting to Filaments Improved Adhesion to Plastics, Elastomers or Polymers

Industrial Rayon Corpn. *USP* 2,862,281

The material is treated with an isocyanate reaction product which decomposes to yield an isocyanate at > 105°c. Thus viscose rayon yarn is treated with the reaction product of 1,6-hexane diisocyanate with diethyl malonate, dried, made into fabric, coated with uncured rubber stock and then cured under pressure at 130–180°c. C.O.C.

Bonded Fibre Fabric Resembling Leather

DuP *BP* 811,444

Fabric resembling leather both in appearance and in its permeability to water vapour is obtained by treating a batt consisting mainly of polyester filaments with the polymeric reaction product of a polyalkylene ether glycol, an organic di-isocyanate and a chain-extending compound containing active H atoms, e.g. water, H_2S, or an organic compound containing active H atoms attached to two different atoms in the molecule, e.g. hydrazine [*sic*]. C.O.C.

Variegated Colour Coating of Cloth or Plastic Sheeting

Edmont Manufacturing Co. *USP* 2,859,730

Apparatus embodying a knife coater to which the coating material is supplied in various colour combinations. These combinations can be varied from time to time according to the pattern it is desired to produce. C.O.C.

Wrinkle Finish on Paper, Cloth, Plastic Sheeting or the like

Commonwealth Engineering Co. of Ohio *USP* 2,862,835

Cloth or similar sheet material is coated with a liquid wrinkle finish, and then while supported on a metallic design both the cloth and the metallic design are heated while the latter is supported by an insulating material that does not absorb heat. This results in a second and different wrinkle pattern being imposed on the wrinkle pattern formed by the wrinkle finish. C.O.C.

Metallised Fibres, Yarns, and Fabrics

Commonwealth Engineering Co. of Ohio *USP* 2,862,783

The fibres are treated with a heat-decomposable gaseous metal compound. Thus continuous filaments formed from a volatile organic solvent solution of the fibre material are dried by heat to drive off all the solvent and are then immediately treated at 250–450° F. in an atmosphere containing a carbonyl of Ni, Fe, Cr, Mo, Co or Sn. C.O.C.

Laminated Fabrics

A. Felix and J. J. Horn *BP* 811,931

Two plies of fabric have an interlining of fabric, coated on one or both sides with polyethylene, inserted between them. The assembly is then heated and pressed to cause penetration of the polyethylene into the interstices of each fabric without rendering them impervious to air and water vapour. C.O.C.

Fibre-reinforced Plastic Sheeting

DuP *BP* 811,637

A corded lap of polymeric synthetic fibres is bonded together with an elastomeric butadiene–acrylonitrile copolymer. The product has the chemical resistance, pliability and extensibility of a continuous plastic film together with the high strength of a woven heavy duty fabric. They have high strength at low weight and uniform strength and extensibility in all directions. C.O.C.

Transfer Paper, Typewriter Ribbons, etc. (V p. 325)
Fibre Structure and Mechanical Properties of Untreated and Modified Cotton (VI p. 325)
Effect of Mercerisation on Resistance of Cotton to Micro-organisms (VI p. 325)
Mechanical Properties of Cotton treated with Ethylamine or with Mercerising Caustic (VI p. 325)
Regenerated Cellulose of Improved Resistance to Sunlight (VI p. 327)
Interaction between Cellulose and Formaldehyde—Review of Literature (XI p. 336)
Titanium Dioxide as a Catalyst for Damage of Cellulose by Light (XI p. 337)
Heating of Thermoplastic Synthetic Materials (XIII p. 340)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Fluorescent Brightening Agents in the Paper Industry and their Evaluation

A. Berger and H. Unterbirker

Das Papier, **13**, 5–12 (Jan. 1959)

The whiteness of a paper can be increased by bleaching, filling, nuancing, and fluorescent brightening agents. The eye is more sensitive to "whiteness" than to "brightness". Curves show the effect of various Blankophors on bleached sulphite pulp. The fact that sized papers require larger doses of fluorescent brighteners than unsized paper is due to the size absorbing ultraviolet radiation, as well as short-wave blue light, thus depriving the brightening agent of its excitation energy. R.A.

Rate of Decomposition of Ethyl Xanthate in Caustic Soda Solution

M. Wroński

Faserforsch. und Textiltech., **10**, 46–47 (Jan. 1959)

The decomposition of ethyl xanthate in caustic soda solution may be represented by a first-order equation. The velocity constant k depends on the concentration of NaOH and on the ionic strength μ, according to the relation—

$$\log k = \log k_0 - m\mu$$

where m is a constant. Measurements of k_0 at 25° and 35°c. give an activation energy of 19·8 kcal./mole. W.R.M.

Chemistry of Xanthates and Viscose

VII—Study of the Polymeric Sulphur Compounds and the Composition of Viscose with Labelled Atoms

S. N. Danilov, N. F. Gintse, and K. V. Levitskaya

Zhur. obshch. khim., **28**, 2948–2958 (Nov. 1958)

Using labelled sulphur (^{35}S) and the usual analytical procedures the investigation of the fission of sulphur from dixanthates of cellulose and ethanol and from sodium disulphide and perthiocarbonate is carried out. This procedure could also be used in connection with the changes which occur during the ageing of viscose.

IX—Detection and Rôle of Polysulphides in Viscose

S. N. Danilov, N. F. Gintse, and M. G. Okun'

Ibid., 3192–3202 (Dec. 1958)

The potentiometric estimation of polysulphides in viscose, normally a very difficult process, is somewhat simplified by treatment with activated charcoal and anionic resins. The optical density values for viscose and for trithiocarbonate in alcoholic soln. are analogous. In aq. soln. trithiocarbonate undergoes oxidative hydrolysis to sodium disulphide. The existence of large amounts of trithiocarbonates and of small amounts of perthiocarbonate in soln. of viscose is noted. G.J.K.

Relative Participation of Carbon Disulphide in the Main and Side Reactions for Viscose Formation at Low and at Normal Temperatures

E. A. Abramova

Zhur. obshch. khim., **28**, 3217–3219 (Dec. 1958)

At temp. around 0°c. the formation of cellulose xanthate groups by the reaction of cellulose with CS_2 in alkaline medium is increased to a considerable extent relative to the same reaction being carried out at normal temp. (15–30°c.). Decrease in concn. of alkali opposes this increase. G.J.K.

X-Ray Small-angle Scattering of Cellulose Fibres
I—Concept of Scattering Power and a Method for its Determination in Electron Units
D. Heikens *J. Polymer Sci.*, **35**, 139–143 (Feb. 1959)
II—Scattering Power of Various Cellulose Fibres
P. H. Hermans, D. Heikens, and A. Weidinger
Ibid., 145–163

Cellulose Monofilaments—Strain Dependence of Stress Relaxation
E. Passaglia and H. P. Koppehele
J. Polymer Sci., **33**, 281–289 (Dec. 1958)

Stress-relaxation behaviour of isotropic and oriented cellulose filaments were studied at 25°c. and 50°c. and 50% R.H. at strains between 0·5 and 5%. Log (modulus)–log (time) curves were found to be different at different strains, but superimposable by translation along the log (time) axis. In general, the relaxation of isotropic filaments is much faster than that of oriented filaments. P.T.S.

Hydrogen Bonds in Native Cellulose
C. Y. Liang and R. H. Marchessault
J. Polymer Sci., **35**, 529–531 (March 1959)

Infrared dichroism of OH stretching frequencies suggests hydrogen bonding between the C_3 hydroxyl group of one glucose residue and the ring oxygen atom of the next residue is responsible for the 3350 cm.$^{-1}$ absorption frequency. Also, hydrogen bonding between the C_6 hydroxyl group of one residue and the bridge oxygen atom of the neighbouring chain may be responsible for the absorption frequencies at 3305 and 3405 cm.$^{-1}$. Other assignments of infrared absorption frequencies are discussed and compared with the assignments of other workers. P.T.S.

Moisture Relations of Cellulose. IV—Effect of Stabilisation of Cotton Cellulose on its Sorptivity at Different Temperatures, and its Bearing on Isosteric Heats of Sorption
M. Wahba, S. Nashed, and K. Aziz
J. Textile Inst., **49**, T 519–T 531 (Nov. 1958)

Adsorption–desorption cycles were carried out from dryness to saturation with unstabilised cellulose at 15°, 30°, and 40°c., and with cellulose stabilised by repeated drying and wetting at 0°, 15°, 27·5°, 40°, and 50°c. Stabilisation of the cellulose makes the sorption isotherms reproducible, and in general lowers the sorptivity of the cellulose. The binding energy of the chain molecules in the non-crystalline region of cellulose varies with temperature. The Clausius–Clapeyron equation cannot be used to determine the heats of sorption or desorption because the area of the sorbing surface changes with temperature. P.T.S.

Recrystallisation of Cellulose
I. I. Korol'kov, V. T. Sharkov, and A. V. Krupnova
Zhur. priklad. khim., **31**, 1560–1565 (Oct. 1958)

The proportion of amorphous cellulose in viscose rayon can be increased by stretching it in the coagulating bath. Recrystallisation is favoured by heating cellulose in water at a higher temp. which causes splitting of the macromolecules, thus making possible solid repacking of their components. Recrystallisation takes place in two phases. At a lower temp. hydrogen bonds between the chains are broken and at a higher temp., when the D.P. is decreased and 2·5–5% loss in wt. is observed. Cellulose, which is regenerated from its aq. soln. or ground, hydrolyses 3–5 times as fast as wood cellulose. T.Z.W.

Cellulose and its Principal Derivatives—Relation between Intrinsic Viscosity and Degree of Polymerisation
R. J. E. Cumberbirch and W. G. Harland
J. Textile Inst., **49**, T 679–T 686 (Dec. 1958)

If a relation can be established between intrinsic viscosity and D.P., then it is much simpler and more convenient to determine D.P. from intrinsic viscosity than from time-consuming direct D.P. methods. The intrinsic viscosity of cellulose triacetate was measured in a methylene chloride–ethanol mixture, and the equation—

$$\text{Intrinsic viscosity} = 0{\cdot}0156(\text{D.P.})^{0{\cdot}824}$$

was shown to hold under the experimental conditions specified. The intrinsic viscosity of saponified secondary acetates was measured in cuprammonium solutions, and the equation in this case is—

$$\text{Intrinsic viscosity} = 0{\cdot}0319(\text{D.P.})^{0{\cdot}667}$$

For cellulose nitrate in n-butyl acetate,

$$\text{Intrinsic viscosity} = 0{\cdot}0141(\text{D.P.})^{0{\cdot}909}$$

In these relations, which have the general form—

$$\text{Intrinsic viscosity} = K(\text{D.P.})^{a}$$

a is a measure of molecular coiling in solution—the greater a, the more extended is the cellulose chain in solution. P.T.S.

Cellulosic Fibre Heats of Sorption deduced from Calorimetric Measurements
D. N. E. Cooper and D. K. Ashpole
J. Textile Inst., **50**, T 223–T 232 (Feb. 1959)

If q_c is the heat of wetting of a cellulosic fibre at regain c (the heat evolved per gram of dry fibre when it is completely saturated by immersion of the fibres conditioned to regain c in liquid water), and q_0 is the heat of wetting from dryness, then—

$$q_c = q_0 \exp(-ac)$$

where a is a constant for a particular fibre, but varies from fibre to fibre. The differential heat of sorption (Δh_c) is the heat evolved when one gram of liquid water is absorbed by an infinite mass of fibres at regain c. The variation in a from fibre to fibre suggests that there are differences in the differential heats of sorption, but not necessarily differences in the energies of the water–cellulose bonds. The differential heat of sorption gives information about the absorbing regions of the fibre; the heat of wetting is controlled by the proportion of the fibre accessible to water. The differential heat of absorption is related to a and q_c—

$$\Delta h_c = 100aq_c$$

q_0 is also related to a—

$$100a = a_0 + a_1q_0 + a_2q_2$$

where a_0, a_1, and a_2 are empirically determined constants: q_0 can thus be found by an indirect method, and—

$$\Delta h_0 = 100aq_0$$

P.T.S.

Cellulosic Fibres—Changes in Fine Structure during Mild Acid Hydrolysis
W. B. Achwal, E. H. Daruwalla, G. M. Nabar, and P. Subramaniam *J. Polymer Sci.*, **35**, 93–112 (Feb. 1959)

The results of mild acid treatment on standard cellulose, cellulose mercerised with and without tension, viscose rayon, and cuprammonium rayon were studied via changes in degree of polymerisation, fibre density, crystallinity, moisture regain, oxidative susceptibility, and equilibrium dye absorption. The mild acid action (7 N. sulphuric acid, 30°c., 4–900 hr., liquor ratio 50:1) takes place in three stages, each one slower than the previous one. It is suggested that changes in properties are caused by solution of a hydrolysable fraction and crystallisation of the remaining cellulose chains. P.T.S.

Interaction between Cellulose and Formaldehyde—Review of the Literature
W. J. Roff *J. Textile Inst.*, **49**, T 646–T 663 (Dec. 1958)

After a historical introduction to the subject, this paper discusses the conditions under which formaldehyde can react with cellulose, the chemical changes involved and the evidence that they do in fact take place, and the effect on the properties of cellulose of the reactions. 74 references. P.T.S.

Oxidation of Hydrocelluloses by Chlorous Acid
A. Meller *J. Textile Inst.*, **50**, T 237 (Feb. 1958)

G. F. Davidson and T. P. Nevell (cf. J.S.D.C., **74**, 70 (1958)) showed that terminal aldehyde groups of the molecular chains in hydrocelluloses cannot be quantitatively converted to carboxyl groups by oxidation with acidified chlorite solution, and thus the method is not suitable for determination of aldehyde groups in hydrocelluloses. In the present Letter to the Editor the author points out a publication by himself overlooked by Davidson and Nevell (*Tappi*, **38**, 682 (1955)).

G. F. Davidson and T. P. Nevell *Ibid.*, T 238–T 239

The authors reply to the criticism of Meller (above) and discuss the relative merits of the copper number test and the alkali solubility test as a measure of the oxidation of aldehyde end-groups to carboxyl groups. P.T.S.

Influence of the Cellulose Material on the Formation of Alkali Cellulose
B. Philipp, R. Lehmann, and C. Ruscher
Faserforsch. und Textiltech., **10**, 22–35 (Jan. 1959)
The action of alkali at different NaOH concentrations on a number of soluble pulps is studied by measurement of uptake of NaOH, change in X-ray diagram, and the amount of insoluble residue left after xanthation. The suitability of these methods of estimating pulp reactivity is discussed, and a classification of sulphite pulps according to their behaviour on alkali treatment is suggested.
W.R.M.

Titanium Dioxide as a Catalyst for Damage of Cellulose by Light
J. Schurz and E. Kienzl
Faserforsch. und Textiltech., **9**, 513–519 (Dec. 1958)
The catalytic effect of TiO_2 on the photodegradation of cellulose is briefly discussed and a possible mechanism suggested. Oxidation is greatest when light of wave-number about 3500 mm.$^{-1}$ and over is used. TiO_2-catalysed oxidation of some dissaccharides is described, and also some preliminary experiments on the photo-oxidation of cellulose.
W.R.M.

Cotton Cellulose Copper Absorption from Sodium Cuprate Solutions— the Normann Compound
G. F. Davidson and H. Spedding
J. Textile Inst., **49**, T 621–T 626 (Nov. 1958)
Cellulose will take up copper from a solution of cupric hydroxide in sodium hydroxide. The ion $Cu(OH)_4^{2-}$ is probably involved, and several workers found a ratio of approx. 0·5 copper atom per glucose unit at the maximum uptake, and thus a definite compound was suggested, first by Normann. The experiments described in this paper show that the amount of copper taken up by cotton cellulose increases continuously as the copper concentration in the solution increases. It appears to approach asymptotically a value in excess of the copper concentration necessary to form the Normann compound.
P.T.S.

Catalytic Action of Copper on the Alkaline Autoxidation of Cellulose
R. I. C. Michie and S. M. Neale
Nature, **183**, 534–535 (21 Feb. 1959)
Copper is found to have an unexpectedly high catalytic effect on the reaction of cellulose with oxygen at low alkalinities. The rate of alkaline autoxidation is proportional to the concentration of NaOH below 5 N. The catalytic activity of the copper at low NaOH concn. is estimated to be greater than that of other metals at high NaOH concn. It is suggested that at high alkali concn., as the concn. of catalyst is increased, the reaction rate may depend on the availability of oxygen and thus be eventually independent of the concn. of catalyst. This limitation is less likely to apply in the case studied, where the rates of reaction are relatively low.
W.R.M.

Cellulose II— Morphology and Reactivity. The Reactivity of Primary and Secondary Hydroxyl Groups during Heterogeneous and Homogeneous Acetylation
H. Krässig and E. Schrott
Makromol. Chem., **28**, 114–139 (Oct. 1958)
In heterogeneous acetylation the ratio of free primary to free total hydroxyl groups remains constant at 1 : 3 at first, and then decreases. In homogeneous acetylation preferential reaction with the primary hydroxyl groups occurs from the start of the reaction. Primary hydroxyl groups are thus more reactive than secondary. If, however, diffusion is the rate-controlling step, not hydroxyl reactivity, it is suggested that primary and secondary hydroxyl groups will react in the ratio in which they are present in the cellulose. Alternatively the apparently equal rates of reaction of primary and secondary hydroxyl groups in the heterogeneous reaction may be because secondary hydroxyl groups may be hydrogen-bonded in a different way from primary hydroxyl groups.
P.T.S.

Formation of Peroxides during the Oxidation of Cellulose Ethers
O. P. Koz'mina, V. I. Kurlyankina, E. N. Matveeva, and M. K. Aleksandrovich
Zhur. obshch. khim., **28**, 3202–3205 (Dec. 1958)
The oxidation of cellulose ethers, with the formation of peroxides, by atmospheric oxygen in the presence of ultraviolet radiation is investigated. The presence of acetates of copper and iron strongly retards the rate of oxygen uptake of ethylcellulose. Mere pretreatment of an aged soln. of ethylcellulose with these salts has only a small protective effect.
G.J.K.

Degree of Polymerisation and its Distribution in Cellulose Rayons. VII— Intrinsic Viscosity and Degree of Polymerisation of Secondary Cellulose Acetate Fractions
R. J. E. Cumberbirch and W. G. Harland
J. Textile Inst., **49**, T 664–T 678 (Dec. 1958)
Little is known about the effect of range and distribution of D.P. on the mechanical properties of rayon fibres, and the work described here has as its ultimate aim some correlation between these properties. The fractionation of secondary cellulose acetate was carried by dissolving in a methylethyl ketone–acetone solvent, cooling and adding small quantities of benzene, collecting a fraction at each stage. The intrinsic viscosities of the fractions were measured in an 80 : 20 (by vol.) acetone–water mixture to minimise dilution of acetone (if pure acetone were used as the solvent) by water from the cellulose, and to hinder any tendency of polymer molecules to associate in solution. D.Ps. of the fractions were measured osmotically and no difference in result was found when three different solvents were used. The constants K and a in the equation—

$$\text{Intrinsic viscosity} = K(\text{D.P.})^a$$

are very sensitive to slight variations in D.P. or intrinsic viscosity, but for any chosen values of K and a the equation is reasonably satisfactory.
P.T.S.

New Paths for the Synthesis of Simple Cellulosic Ethers
E. A. Plisko
Zhur. obshch. khim., **28**, 3214–3216 (Dec. 1958)
Alkylation of cellulose in alkaline media has been carried out using methyl- and ethylesters of *p*-toluene sulphonic acid, the diethylester of toluene-disulphonic acid, methyl-, ethyl-, *n*-propyl-, and *n*-butylesters of benzenesulphonic acid, and the methyl and ethyl esters of naphthalene-*a*-sulphonic acid. Alkylation occurs more readily in organic bases than in aq. alkaline hydroxide. In the latter solvent, methylation occurs most readily, being followed in decreasing order by ethylation and propylation etc. The presence of an additional alkyl sulphonic acid ester grouping in the alkylating molecule decreases the rate of alkylation.
G.J.K.

S. N. Danilov's Investigations of Cellulose and its Esters
E. A. Plisko, M. G. Okun', N. M. Grad, and N. F. Gintse
Zhur. obshch. khim., **28**, 3174–3184 (Dec. 1958)
A review of the work carried out since 1917 by Danilov and his collaborators in this field is given, and a comprehensive bibliography (141 references) is available.
G.J.K.

Anhydro, Desoxy, and Unsaturated Derivatives of Polysaccharides
S. N. Danilov and A. A. Lopatenok
I— Desoxycellulose from Cyanoethoxycellulose
Zhur. obshch. khim., **28**, 3184–3188 (Dec. 1958)
Interaction of metallic sodium with cyanoethoxycellulose brings about the complete elimination of cyanoethoxy groups (partly in the form of acrylic acid) and allows the formation of the methylene, or, in part, the methyl group in the glycosidic linkage, i.e. allows the formation of desoxycellulose. In part, the fission of the cyanoethoxy group leads to the formation of desoxy group, and in part to the formation of acrylonitrile due to the reversibility of this reaction in alkaline media. The presence of the desoxy group in the product has been confirmed by analysis of the product itself and of its nitrate and acetate derivative.
II— Synthesis of Anhydrocellulose from *p*-Toluenesulphonic Esters *Ibid.*, 3189–3191
The action of sodium in liquid ammonia on the *p*-toluenesulphonic acid esters of cellulose (I) allows the formation of anhydrocellulose the composition of which has been proved by analysis. For esters of this kind which have more than 1 ester grouping to each glycoside linkage the reaction with sodium in liquid ammonia involves not only the formation of anhydro rings but also involves hydrolysis.
G.J.K.

Mixed Esters of Cellulose
W. Voss and H. Reimschüssel
Makromol. Chem., **27**, 101–141 (June 1958)

I— Analytical Characterisation
Methods are given for the estimation of bound acetic acid, bound acetic and butyric acids together, free hydroxyl groups, primary hydroxyl groups, and glycol groups in mixed esters of cellulose; and a method of presenting the results is discussed.

II— Preparation and Properties of Mixed Esters of Cellulose
Cellulose triacetate can be partially saponified by aqueous nitric acid. Re-esterification with butyric acid gives a cellulose acetobutyrate. The distribution of the ester groups along the cellulose chains is not random. After reducing the results to a standard cellulose concentration, there is a simple mathematical relationship between the proportion of butyrated and acetylated hydroxyl groups and the specific viscosity, optical rotation, and tensile strength of the esterified cellulose film.

III— Fatty Acid Mixed Esters
For the arguments in the two preceding parts it was essential to confirm that acetyl migration does not occur during the re-esterification of partially hydrolysed cellulose triacetate. This was shown using D-glucose and cellobiose as model compounds and halogenated acetyl groups. P.T.S.

Thermal Oxidation of Benzylcellulose
O. P. Koz'mina and V. I. Kurlyanina
Zhur. priklad. khim., **31**, 1761–1762 (Nov. 1958)
The main products of the thermal oxidation of benzylcellulose are benzaldehyde, benzoic acid, benzyl formate, formic acid, and water. The reaction takes place at 100°C. in an atmosphere of molecular oxygen. T.Z.W.

Carbon-14 Carboxy-labelled Polysaccharides
J. D. Moyer and H. S. Isbell
Bur. Stand. J. Res., **61**, 71–73 (Aug. 1958)
Research Paper 2886
Polysaccharides may be labelled with ^{14}C by treatment with ^{14}C-labelled cyanide. The resulting cyanohydrin yields on hydrolysis a polysaccharide with a ^{14}C-labelled carboxyl group in place of the original reducing end-group. Details are given for the preparation and assay of labelled carboxydextran and carboxyinulin. A.J.

PATENTS

Preventing Slime Formation in the Manufacture of Pulp and Paper
Osakeyhtio Keskuslaboratorio Centrallaboratorium
BP 811,191
The circulating water is treated so that it contains bisulphite anions. The water is best kept at pH 5, sulphurous acid or sodium bisulphite being added to neutral or alkaline water and sodium sulphite to acid water. If necessary other acids or alkalis may be added to bring the water to the desired pH. C.O.C.

Keten Dimer Size for Paper
Hercules Powder Co. *USP* 2,865,743
Uniform distribution of keten dimers in aqueous pulp slurries, and improved retention and sizing, are obtained by (1) dispersing a keten dimer on amorphous silica to form a free-flowing powder, (2) adding this powder to the pulp slurry, and (3) forming the slurry into paper and drying in the usual manner. C.O.C.

Decorative Paper having an Irregular Surface
R. Rubner *USP* 2,861,009
An aqueous dispersion of a plastic is applied in a pattern to the paper which is then brought to $> 100°C$. so as to evaporate off the water rapidly and so cause miniature eruptions in the coated areas. This results in the coated areas having a roughened surface. C.O.C.

Aqueous Coating Compositions for Applications to Fibrous Substrates
Rohm & Haas Co. *BP* 810,575
Compositions which yield clear glossy coatings with no blocking tendencies even under severe temperature and humidity conditions and which are particularly applicable to paper, consist of an aqueous dispersion of (a) a water-insoluble addition polymer of $T_f > 30°C$., e.g. a 64% ethylacrylate 36% methyl methacrylate copolymer, and (b) an ammonium or complex zinc ammonium salt of a linear copolymer of mol.wt. 500–5000 obtained from 1 mol. maleic anhydride and 1 mol. 2,4,4-trimethyl-1-pentene. (T_f is the transition or inflection temperature found by plotting the modulus of rigidity against temperature, cf. Williamson, *British Plastics*, **23**, 87–90, 102 (Sept. 1950)). C.O.C.

Antiseptic Non-woven Cellulose Tissue Handkerchiefs
Vereinigte Papierwerke Schickedanz & Co. *BP* 810,658
Paper handkerchiefs are rendered antiseptic by impregnating them with metallic salts of benzoic acid or chlorinated phenol. C.O.C.

Electrolytic Recording Paper
Faximile *USP* 2,864,748
Paper impregnated with salicylaldoxime and an electrolyte, e.g. KNO_3, is marked brown when an electric current is passed through it via a suitable anode and cathode. C.O.C.

Heat-sensitive Copying Sheets
Minnesota Mining & Manufacturing Co. *BP* 810,863
In copying sheets suitable for use in the process described in *BP* 673,244 heat-sensitivity is obtained by a layer of light-dispersing particles of transparent fusible material. This material must melt to a liquid without volatilisation or decomposition at 60–115°C. It is distributed throughout a thin layer of transparent film-forming organic binder which is infusible at 60–115°C. The fusible material when liquid must have good wetting properties toward the binder and both must have the same refractive index. Thus paper is given a black coating on which is superimposed a layer of cadmium stearate and rubber from dispersion and solution respectively in heptane. Heating the treated material to above the m.p. of cadmium stearate renders the heat-sensitive layer transparent and allows the black undercoat to become permanently visible at the heated area. C.O.C.

Transfer Paper, Typewriter Ribbons, etc. (V p. 325)
Transfer Sheet or Carbon Paper containing a Metallic Salt and a Hydrotrope (IX p. 331)
Wrinkle Finish on Paper, Cloth, Plastic Sheeting or the like (X p. 335)
Fumaric Polyesters as Plasticisers and Gelling Agents (XIII p. 340)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Fast Dyeing of Glove and Garment Leathers
E. Lüscher *Leder*, **9**, 115–121 (1958): *J. Amer. Leather Chem. Assocn.*, **54**, 49 (Jan. 1959)
Dyes for leather that would enable the leather to compete with substitutes on an equal basis as regards levelness of colour and fastness to washing and light have either not been available or have been too costly. Derma Echt CW and W (S) dyes are fast to light and washing, and are used like anionic dyes but are fixed more rapidly, so that only about one-quarter as much acid is needed. Acetic acid is to be preferred, but if this does not exhaust the bath, formic acid should be added. An aftertreatment with a cationic fixative is required; this may be Dermafix LW (which contains copper) or a copper salt such as copper sulphate. These dyes are especially good for surface-dyeing glove leather which is to be coloured on one side only; the dye on one side can easily be buffed off. Formerly such leather was dyed by brushing. C.J.W.H.

Keratin— Stress Relaxation and Diffusion
J. E. Algie *J. Polymer Sci.*, **35**, 535–536 (March 1959)
The rate of stress decrease or increase in a stretched horsehair following a change in R.H. is diffusion controlled. P.T.S.

Architecture of a Protein Molecule
J. C. Kendrew *Nature*, **182**, 764–767 (20 Sept. 1958)
Brief review of the structure of proteins and in particular of myoglobin. Myoglobin consists of 153 amino acids in a single chain and is spherical; hence, the α-helix must be folded upon itself. A major advance in technique has been to use long wavelength X-rays ($\lambda = 6A.$). These do not permit resolution of individual atoms, so that the α-helix appears as a rod, but the contortions of the rod are relatively easy to follow. By using a combination of the

heavy atom technique and low resolution X-ray analysis the general architecture of the molecule has been deduced. E.V.T.

Lanthionine combined in Peptides as a Source of Labile Sulphur

H. Zahn and H. J. Kessler

Makromol. Chem., **27**, 218–241 (July 1958)

The syntheses of diglycylmesolanthionine, mesolanthionyl-diglycine, and diglycylmesolanthionyldiglycine are described. The thio-ether linkage of lanthionine derivatives with peptide bonds is not stable in alkali, and as in the case of cystine hydrolysis, a hydrogen ion is lost from the β carbon atom. Lanthionine combined in proteins is unstable in alkali. Evidence is adduced for the hypothesis that the micelles of wool are bound together by a sulphur-rich cement. P.T.S.

Reactions of Thiosulphate with Cysteine

T. W. Szczepkowski *Nature*, **182**, 934–935 (4 Oct. 1958)

Thiosulphate reacts spontaneously with cysteine *in vacuo*. Slight excess of thiosulphate was mixed with cysteine buffered to pH 7–7·4 and allowed to stand overnight. H_2S was evolved and was trapped in a solution of $Ca(OH)_2$, and cysteine was precipitated. Radioactive labelling shows that the sulphur in the H_2S originates only from the thiosulphate. Glutathione and dimercaptopropanol react in the same way. When the solution containing the cysteine precipitate is warmed, the cysteine redissolves and cysteinethiosulphonic acid $R{\cdot}S{\cdot}S{\cdot}SO_3H$ is formed. With tetrathionate, cysteine is thought to form cysteinedithiosulphonic acid $R{\cdot}S{\cdot}S{\cdot}S{\cdot}SO_3H$. E.V.T.

PATENTS

Treating Hides and Skins with Resin Dispersions

ICI *BP* 811,694

Treatment with an aqueous dispersion of a water-insoluble solid copolymer of a methacrylic acid and an aldehyde both fills and tans to yield a full, light coloured leather having good drying properties. C.O.C.

Finishing Leather with Polyamides

BASF *BP* 811,696

Supple and elastic coatings are obtained on leather by use of polyamide compositions containing no softener if the polyamides are obtained by the copolymerisation of linear polyamide-forming compounds of (1) the diamine-dicarboxylic or aminocarboxylic acid types, and (2) the diamine-dicarboxylic acid type in which the carboxylic groups are connected by a chain of 6–12 C which chain has a lateral branch of 7–10 C. Thus a salt of 4,4′-diaminodicyclohexylmethane and 1-octylnonane dicarboxylic acid (1·9) is condensed with caprylic lactam and hexamethylene diamine adipate to yield a transparent product which readily dissolves in alcohol to yield solutions compatible with ethyl acetate and solutions of cellulose nitrate in ethylacetate, and also with acetone and etherified urea resins dissolved in butanol. C.O.C.

XIII— RUBBER; RESINS; PLASTICS

Static Electricity in Polymers. I— Theory and Measurement

V. E. Shashoua *J. Polymer Sci.*, **33**, 65–85 (Dec. 1958)

The Static Propensity Tester will measure the rate of build up of charge when a polymer film or fabric is charged by electrodes to potentials in the same range as those developed through friction— 3,000–6,000 v. It will also measure the rate of charge decay. The rate of charge decay depends on the exposed area of the sample and its electrical resistance. The rates of decay of positive and negative charges in samples are not necessarily the same. The logarithm of the rate of charge decay is proportional to the applied voltage and to the relative humidity of the atmosphere surrounding the sample. For wool, the relative rates of decay of negative and positive charges vary depending on the previous history of the wool. This anomalous behaviour may be caused by surface impurities. P.T.S.

Formation of Polyamide Resins. VII— Composition and Structure of Salts from Dicarboxylic Acids and Diamines or Hydrazine

A. S. Shpital'nyĭ and Ya. A. Kharit

Zhur. obshch. khim., **28**, 2687–2693 (Oct. 1958)

In the case of salts of diamines or hydrazine with azelaic and sebacic acids a constant composition (equimolecular proportion of acid and base) is achieved irrespective of the relative concn. of the reacting entities. On the other hand, salts obtained from reaction of hydrazine with short-chain dicarboxylic acids, e.g. succinic or adipic acids, vary in constitution dependent upon whether hydrazine is present in excess. Excess hydrazine causes the formation of a salt containing 2 moles of hydrazine to 1 mole of dicarboxylic acid (succinic or adipic acids only). In aq. soln. of its salts, with dicarboxylic acids, hydrazine behaves as a monovalent base. An analogous situation evidently occurs in polyamide resins. G.J.K.

Effect of Compounds of Low Molecular Weight on the Photochemical Degradation of Polyethylene Terephthalate

V. V. Korshak, K. K. Mozgova, and A. P. Zasechkina

Zhur. obshch. khim., **28**, 2847–1853 (Oct. 1958)

The photochemical degradation of polyethylene terephthalate, into which low-mol.wt. compds. have been introduced, is investigated in the ultraviolet region. The low-mol.wt. compds. (salol, diethyl ester of dihydroxy terephthalic acid, β-methyl-umbelliferone and 2-*o*-hydroxy-benzoxazole) are introduced into the polymer from a mixed Chlorex*-ethanol solvent, the latter acting as a swelling agent for the polymer. Photochemical degradation (as shown by the change in the physical properties, i.e. loss of elasticity, decrease in breaking strength and decrease in mol.wt. from 140,000 to 12,000) occurs more readily when a broad range ultraviolet lamp is used than when a limited range (300–320 mμ.) is used. The low-mol.wt. compds. themselves absorb in the ultraviolet region. The effects of the addition of these compounds on the properties of the polymer, both before and after irradiation, differ depending on the compound added and the results are tabulated. The results so obtained are, in many ways, analogous to those obtained for polystyrene. G.J.K.

* Bis-2-chloroethyl ether.

Preparation of Initiated (Seeded) Copolymers from Polyamides and Vinyl Monomers

V. V. Korshak, K. K. Mozgova, and M. A. Shkolina

Doklady Akad. Nauk S.S.S.R., **122**, 609–611 (1 Oct. 1958)

The formation of a limited surface film of polystyrene (or polymethyl methacrylate) on the polyamide fibre is explained in terms of initial ozonolysis (with the intermediate formation of the hydroperoxide) and subsequent reaction with the vinyl monomer—

$$-[CH_2]_n-CO{\cdot}NH-[CH_2]_n \xrightarrow{O_2} -[CH_2]_n-CO-\underset{\displaystyle OOH}{\underset{|}{N}}-[CH_2]_n-$$

$$\xrightarrow{R{\cdot}CH:CH_2} -[CH_2]_n-CO-\underset{\displaystyle OCH_2-CH-R}{\underset{|}{N}}-[CH_2]_n-$$

such surface film is limited to a 20% increase in weight and results in a decrease in wettability with ethanol. This reaction has been carried out on Capron and Amid G–669. Appreciable changes in the tensile strength of the fibre occur only on prolonged (> 30 min.) ozonolysis. G.J.K.

PATENTS

Printable High-density Polyethylene Film

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Printable film can be produced from high-density polyethylene of the type described in *BP* 639,306 if the polyethylene is extruded at < 325°c. This is a critical temperature above which the polyethylene can be formed into films which are printable and yet have good surface properties, i.e. the surface either has acceptable slip and will not block or else it can be easily brought to this condition by applying a size. C.O.C.

Lead Chloride–Lead Silicate Complexes as Stabilisers for Vinyl Resin Compositions

National Lead Co. *BP* 810,578

Basic lead chloride–lead silicate complexes, e.g. those described in *USP* 2,379,270, are excellent stabilisers for vinyl halide resin compositions. C.O.C.

Improving the Printing and Coating Properties of Plastic Materials
Modern Plastic Machinery Corpn. *USP* 2,864,755

Plastic sheeting or the like (plastic of any type, e.g. polyethylene, polyester, nylon, polyvinylchloride) has one face in contact with a dielectric material and the other face in contact with an electrode. A pulsating or variable electric field is established direct in part at least from the dielectric toward the plastic. This results in the face next to the dielectric material becoming receptive to printing inks and coating compositions, the other face remaining unaltered in its properties.

USP 2,864,756

A DC electric field is established at the surface of a plastic sheet, particularly one of polyethylene, and then the intensity of this field is alternately varied between points below and above the gaseous discharge part of the atmosphere about the surface being treated. C.O.C.

Plastic Film as Substitute for Tracing Cloth
E. Gronwall *BP* 812,099

One side of a transparent polyethylene terephthalate film is blasted with a hard powder of particle size 0·05–0·005 mm. C.O.C.

Polyethylene Films of Improved Clarity and Transparency
Distillers Co. *BP* 811,776

Linear polyethylene of density $< 0{\cdot}95$ is mixed with a liquid to form a solid, homogeneous composition. This is formed into a film and is stretched below the softening point of the polyethylene to give the desired transparency. C.O.C.

Condensates of Epoxidised Fatty Esters with Amine Compounds
Coates Brothers & Co. *BP* 811,797

The condensates of epoxidised fatty esters containing at least one C_{10-22} epoxy-fatty acid residue with a polyamine having primary or primary and secondary amino groups or an amino alcohol containing at least one primary or secondary amine group and at least one primary or secondary alcohol group, are more or less resinous materials of use in paints, printing inks, etc. C.O.C.

Heating of Thermoplastic Synthetic Materials
K. H. Steigerwald *BP* 811,844

The materials are irradiated for a short time with charged particles of high beam density and given physical treatment, e.g. stretching to orient the molecules, during that period. C.O.C.

Fumaric Polyesters as Plasticisers and Gelling Agents
C. F. Roser *BP* 811,946

Polyesters prepared from diols and, at least in part, from fumaric acid are good plasticisers and gelling agents for poly(vinylchloride), vinylchloride copolymers, and cellulose nitrate. They have no tendency to migrate or be removed by hydrocarbon solvents. C.O.C.

Effect of the Chemical Composition of Reagents on the Bonding Strength of Viscose Rayon Cord to Rubber (VI p. 326)
Wrinkle Finish on Paper, Cloth, Plastic Sheeting or the like (X p. 335)
Fibre-reinforced Plastic Sheeting (X p. 335)

XIV—ANALYSIS; TESTING; APPARATUS

Determination of the Molecular Weight of Polyethylene Terephthalate
A. Conix *Makromol. Chem.*, **26**, 226–235 (May 1958)

The number-average molecular weights of unfractionated samples of polyethylene terephthalate were determined via carboxyl and hydroxyl end-group determinations. The polyester is dissolved in hot benzyl alcohol, mixed with chloroform, and titrated with sodium benzylate using phenol red as an indicator. The hydroxyl end-groups are converted to carboxyl groups by reaction with succinic anhydride and estimated as before— the difference between the two titration values gives the hydroxyl end-group content. The relation between intrinsic viscosity $[\eta]$ in a 50:50 phenol–tetrachloroethane solution, and number-average molecular weight $\overline{M}_n$ was found to be—

$$[\eta] = 2{\cdot}1 \times 10^{-4}\overline{M}_n^{0{\cdot}82}$$

Samples of polyethylene terephthalate were prepared in various ways from dimethyl terephthalate and ethylene glycol and from monoglycol terephthalate. *In English.* P.T.S.

Age and Colour Vision
R. Lakowski *Dyer*, **120**, 789–790 (21 Nov. 1958)

The optimum age group for colour perception is 16–35 years, with a rapid deterioration above 55 years. Red–green vision is least affected by age, but with yellow–blue and violet–blue–green deterioration sets in as early as 30 years. A.J.

Visual Pigments in the Colour-blind
W. A. H. Rushton *Nature*, **182**, 690–692 (13 Sept. 1958)

Dichromats confuse red and green, but are of two types— protanopes are insensitive to red and need a very intense red light to match a moderate green, while deuteranopes are nearly normal in their appreciation of brightness. The pigment in the cones of the fovea has been measured by reflection densitometry. Protanopes have only one pigment (chlorolabe) sensitive to the red–green region of the spectrum. Deuteranopes have two pigments photosensitive to this region, the green-sensitive chlorolabe and red-sensitive erythrolabe. Protanopes are insensitive to red because none of their cones contain erythrolabe. Deuteranopes can sense red but cannot distinguish it from green because they have both erythrolabe and chlorolabe in the same cone. Hence, the nervous response from a cone can be stimulated by either red or green light. E.V.T.

Observation of Transient Intermediates in Redox Processes by Oscillo-polarography
W. Kemula and Z. Kublik
Nature, **182**, 793–794 (20 Sept. 1958)

Development of a "hanging" mercury drop electrode enables a clear and stable image to be produced for potentials between 0 and −2v. and currents of any frequency. The normal polarogram for the reduction of *p*-nitroaniline indicates the irreversible reduction—

$$NH_2{\cdot}C_6H_4{\cdot}NO_2 + 6e + 6H^+ \rightarrow NH_2{\cdot}C_6H_4{\cdot}NH_2 + 3H_2O$$

With the present technique the reversible stage—

$$NH_2{\cdot}C_6H_4{\cdot}NH_2 - 2e - 2H^+ \rightleftharpoons NH{\cdot}C_6H_4{\cdot}NH$$

and other unexplained reversible reactions are indicated. E.V.T.

Reactant Resin Condensation on Cotton rapidly Estimated
Chemische Fabrik Pfersee
Melliand Textilber., **39**, 1146 (Oct. 1958)

White cotton finished with dimethylolethyleneurea condensates treated at room temp. for 3 min. with 0·1 N. iodine in KI, rinsed five times, and dried below 100°C. yellows to an extent depending on temp. and time of condensation and on amount of resin. Results are reproducible. Formaldehyde, resin, and catalyst by themselves do not respond. Melamine- and urea-based resins also react, the latter weakly. S.M.J.

Nitration Method for the Intrinsic Viscosity of Cellulose
J. Cyrot *Bull. Inst. Text. France*, (77), 27–54 (Oct. 1958)

Nitric–acetic acid mixtures give better results than nitric–phosphoric acid mixtures. A detailed procedure is described which employs 66 : 34 nitric acid–acetic acid. The cellulose nitrate prepared by this method has an N content of 13·8–13·95% and is stable in solution in butyl acetate. 61 references. J.C.F.

Zirconium Tannage. I—Colorimetric Determination of Zirconium in Leather
D. A. Williams-Wynn
J. Soc. Leather Trades Chem., **42**, 360–368 (Nov. 1958)

Zirconium gives, with sodium alizarinsulphonate, a very intense red colour that is almost specific for Zr; tartrate reduces the colour intensity and stabilises the system against pptn. Sexavalent Cr must be reduced to tervalent, as it greatly increases the absorption density; Ti, Al, and Fe do not interfere. J.W.D.

Colorimetric Estimation of Tryptophan
J. Cegarra and R. Crespo
Investigación e Información Textil, **1**, 264–269 (Oct.–Dec. 1958)

The coloration with *p*-dimethylaminobenzaldehyde was estimated with a Unicam SP 500 and a Hilger Spekker H 760. Beer's law was found to hold good, and the two instruments have good agreement. S.R.C.

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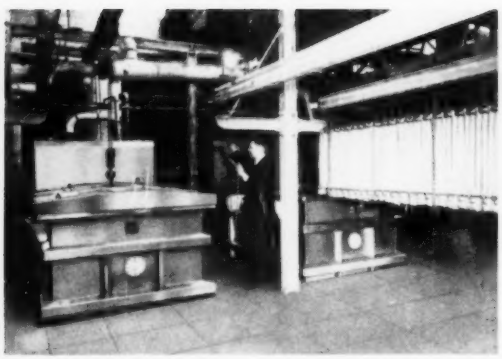

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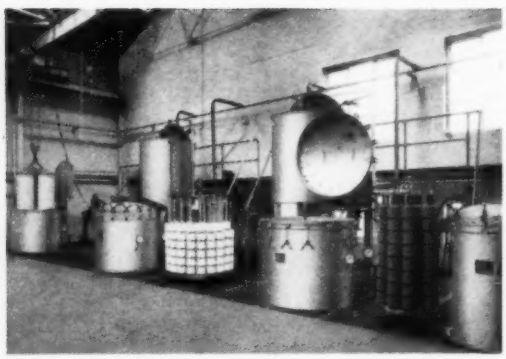

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The post carries membership of the Company's non-contributory pension scheme. In addition a house purchase scheme is in operation.

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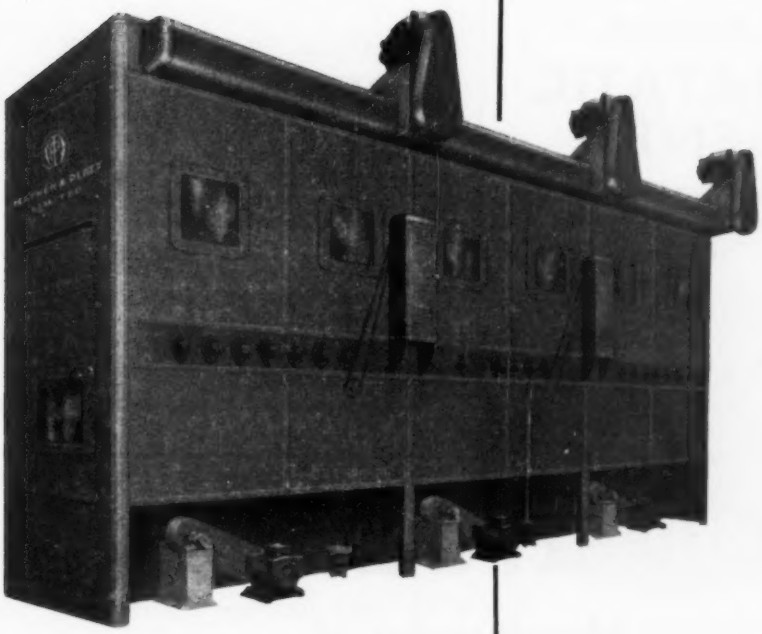

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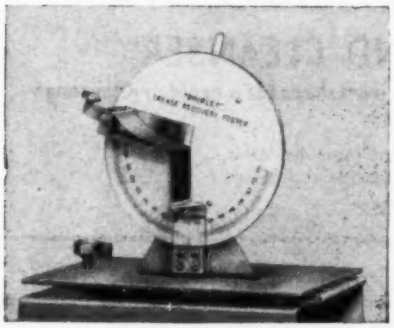

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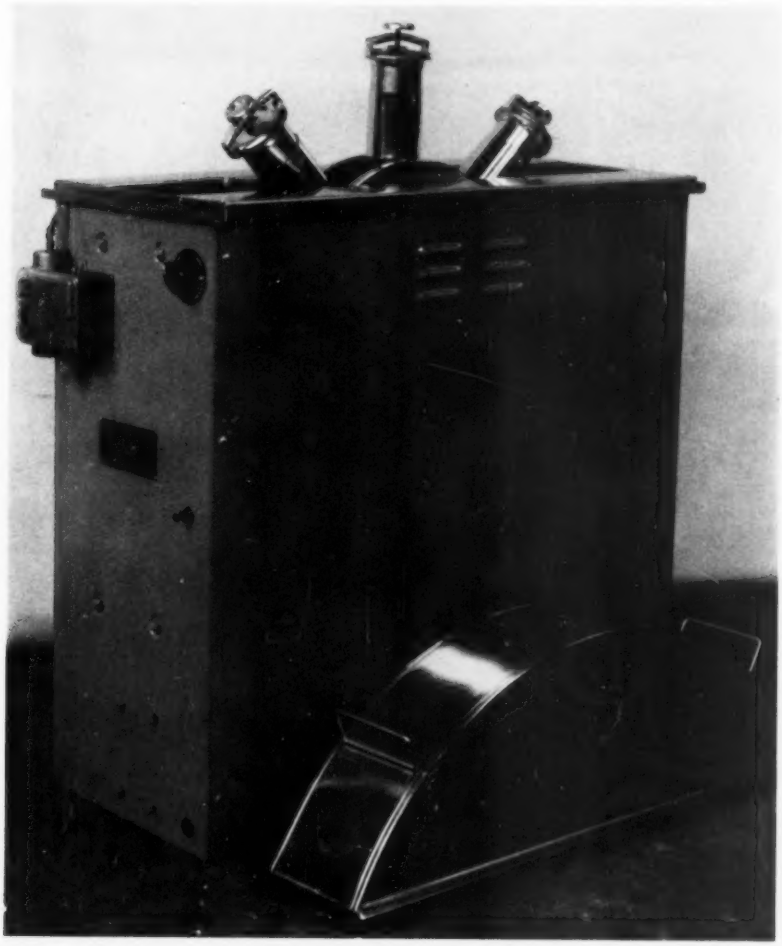

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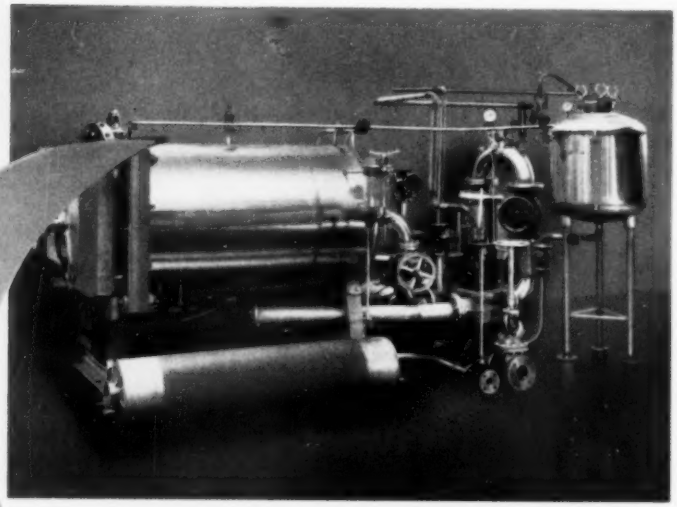

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